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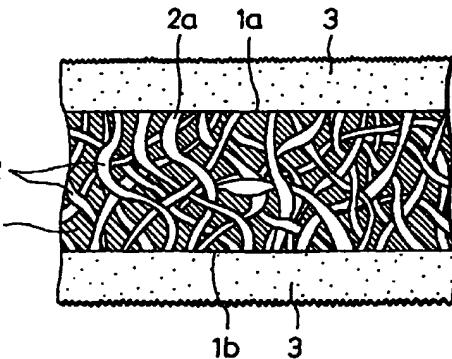
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(54) PROCESS FOR PREPARING POROUS ELECTROLYTIC METAL FOIL

(57) A process for preparing a porous electrolytic metal foil by electrodepositing a metal on a drum cathode by using a drum cathode and an anode to form a metal foil layer and separating the formed layer from the drum cathode, wherein a coating of an electrically insulating material is formed on the cathode surface exposed after the foil separation by subjecting the exposed surface to electrolytic oxidation, by spraying the exposed surface with a resin liquid, or by suspending a machine oil or the like in an electrolyte to deposit the machine oil onto the exposed surface. The metal foil thus obtained has a large number of interconnecting pores in the direction of thickness and, when used as a collector substrate of an electrode for a battery, can prevent the separation of a composite for a battery, thus contributing to an improvement in the cycle time of a battery.

F I G. 2



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Description**TECHNICAL FIELD**

5 The present invention relates to a method of manufacturing a porous electrolytic metal foil and, more particularly, to a method of manufacturing a porous electrolytic metal foil in which when the metal foil is used as a collector of secondary battery, a mixture for electrode can be supported firmly on the collector, and electron transfer reaction can be caused uniformly at the charging/discharging cycle time.

10 BACKGROUND ART

In recent years, as portable electronic equipment such as video cameras and notebook type computers has widely been used, the demand for small high-capacity secondary batteries has increased as power sources therefor. Most of the secondary batteries now being used are nickel-cadmium batteries containing alkali electrolyte, the battery voltage 15 thereof being about 1.2 V. For this reason, a nickel-hydrogen battery has received attention as a higher-power battery, and also a lithium battery has been developed.

The nickel-hydrogen battery works with hydrogen used as an active material for negative electrode. The negative electrode thereof is formed by supporting a hydrogen occlusion alloy capable of reversibly occluding/discharging hydrogen on the collector, and the positive electrode is formed by similarly supporting, for example, nickel hydroxide, which 20 is an active material for positive electrode, on the collector.

For example, when a negative electrode of nickel-hydrogen battery is manufactured, predetermined amounts of hydrogen occlusion alloy powder, conductive material powder such as nickel, and binder powder such as polyvinylidene fluoride are mixed to yield a mixed powder, to which, for example, carboxymethyl cellulose solution is added, by which 25 a slurry, which is a mixture for negative electrode, is prepared. A collector such as a punching Ni sheet with a desirable opening ratio, a Ni foam sheet with a desirable porosity, or a Ni powder sintered body is filled with the slurry. The mixture is supported on the surface of the collector and in the inside voids thereof in a contacting state by sequentially performing drying, rolling, and heat treatment.

When a positive electrode is manufactured, predetermined amounts of nickel hydroxide powder, which is an active material for positive electrode, and a conductive material such as nickel powder are mixed to yield a mixed powder, to 30 which, a predetermined amount of, for example, carboxymethyl cellulose solution is added, and the whole mixture is agitated into a slurry form, by which a mixture for positive electrode is prepared. Thereafter, a collector such as a Ni foam sheet is filled with the mixture for positive electrode. The mixture for positive electrode is supported on the collector by sequentially drying and rolling it.

Lithium batteries are broadly classified into metallic lithium batteries and lithium ion batteries. 35 For the metallic lithium battery, the negative electrode is formed of metallic lithium, and the positive electrode is formed by supporting an active material for positive electrode such as LiCoO₂ on a collector. For the lithium ion battery, the positive electrode is formed in the same manner as described above, but the negative electrode is formed by supporting, for example, carbon (C) capable of occluding/discharging lithium ions on a collector.

In the case of the former battery of the batteries of the two types, dendrite recrystallized lithium is deposited on the 40 surface of metallic lithium, which is the negative electrode, during charging, and it grows as the charging/discharging cycle proceeds, so that the battery cycle life is decreased. In the worst case, the grown recrystallized lithium breaks a separator interposed between the positive and negative electrodes, sometimes causing short circuit.

Thereupon, regarding the lithium battery, the research and development of a lithium ion battery incorporating a negative electrode formed by supporting carbon on the collector is now being carried on. This negative electrode does 45 not present the problem with metallic lithium negative electrode during the charging/discharging cycle.

When a positive electrode of lithium battery is manufactured, predetermined amounts of, for example, LiCoO₂ powder, which is an active material for positive electrode, for example, C powder, which is a conductive material, and, for example, polyvinylidene fluoride, which is a binder, are first mixed to yield a mixed powder, to which a predetermined amount of nonaqueous solvent such as N-methylpyrrolidone is added. The whole mixture is mixed thoroughly, by which 50 a pasted mixture, which is a mixture for positive electrode, is prepared. Then, the mixture is applied onto the surface of collector consisting of metal foil or alloy foil such as Ni, Cu and Ti-Al foil made by, for example, rolling. Thereafter, the mixture for positive electrode is dried to be put on the collector so as to be in firm contact and integral with the collector.

When a negative electrode of lithium ion battery is manufactured, fiber-form, woven cloth-form, or felt-form carbon fiber itself is sometimes used as C. In general, however, predetermined amounts of C powder, the aforementioned 55 binder powder, and nonaqueous solvent are mixed to prepare a pasted mixture for negative electrode, and the mixture is applied to the collector consisting of a metal foil and pressed on it after being dried.

An important point for the aforementioned positive and negative electrodes is that the mixture for positive or negative electrode (hereinafter called the electrode mixture) does not peel off from the collector when the electrode is incor-

porated into a battery at the time of charging/discharging cycle. If the mixture peels off from the collector, polarization begins to increase in the process of charging/discharging cycle, which causes the cycle life characteristics to decrease.

When a Ni foam sheet is used as a collector as in the case of the hydrogen-nickel battery, the electrode mixture is less prone to peel off because it fills the inside of the sheet.

5 However, the pore diameter of such a foam sheet, which is about 100 µm, is too large with respect to the whole sheet. Therefore, although this pore diameter is preferable from the viewpoint of increased filling amount of electrode mixture and useful to prevent the electrode mixture from peeling off, it decreases the mechanical strength of sheet, so that the sheet is prone to be broken. Also, the filling of electrode mixture is nonuniform, so that the electron transfer reaction in the charging/discharging cycle is prone to be nonuniform.

10 When a punching metal sheet, in which openings of a predetermined diameter are formed regularly, for example, in a zigzag lattice pattern, is used as a collector, the opening diameter is too large with respect to the whole sheet as in the case of foam sheet, and in manufacturing, an opening-less sheet must be punched, resulting in an increase in cost.

Sometimes, an expanded metal is used as a collector. To manufacture the expanded metal, a nonporous sheet 15 must be subjected to special fabrication as in the case of the punching metal sheet, so that the cost of expanded metal is higher than that of punching metal sheet.

In the case of the positive or negative electrode for a lithium battery, as described above, a metal foil usually manufactured by rolling is used as the collector, and paste such as an electrode mixture is simply applied to and pressed on the smooth surface thereof, so that peeling occurs easily.

For an electrode in which an electrode mixture is supported on both surfaces of the collector, it is very difficult to 20 apply paste to the completely same thickness on both surfaces. The collector used is generally a rolled nonporous foil, so that lithium ions cannot migrate from one surface of the collector to the other surface thereof.

Therefore, during the charging/discharging, it is impossible to completely use the electrode mixture supported on both surfaces of the collector.

An object of the present invention is to provide a method of manufacturing a porous electrolytic metal foil, in which 25 in manufacturing a metal foil by the electrolytic plating method, the metal foil obtained at the same time when the manufacture proceeds can be made porous.

Another object of the present invention is to provide a method of manufacturing a porous electrolytic metal foil, in which a porous electrolytic metal foil, which is useful as a collector for a secondary battery electrode, is manufactured continuously and in large quantities, and therefore at a low cost.

30 DISCLOSURE OF THE INVENTION

To achieve the above objects, the present invention provides a method of manufacturing a porous electrolytic metal foil, comprising the steps of:

35 continuously forming a metal thin layer by electrically depositing metal ions on the surface of a moving cathode body by an electrolytic reaction which is carried out by immersing an anode body and the moving cathode body in an electrolyte containing metal ions and by applying electric current to between the anode body and moving cathode body while the moving cathode body is moved; and

40 continuously manufacturing an electrolytic metal foil by continuously separating the metal thin layer from the surface of the moving cathode body while the moving cathode body is moved; and further comprising the step of:

carrying out surface treatment of the exposed surface of the moving cathode body exposed after the metal thin layer is separated by wholly or partially forming a film consisting of an electrical insulating material on the exposed surface.

50 FIG. 1 is a schematic sectional view showing a typical cross-sectional structure of a porous electrolytic metal foil manufactured by the method in accordance with the present invention, and FIG. 2 is a schematic sectional view showing a typical cross-sectional structure of an electrode formed by using the metal foil shown in FIG. 1 as a collector and by supporting an electrode mixture on both surfaces thereof.

In these figures, a metal foil 1 is formed with a plurality of open-pores penetrating in the thickness direction from one surface 1a thereof to the other surface 1b, and the metal foil has a porous structure as a whole.

The electrode shown in FIG. 2 has an electrode mixture 3 supported on the surfaces 1a and 1b of the aforesaid metal foil 1. The electrode mixture 3 is supported in such a manner as to get slightly into the open-pore 2 through an 55 opening 2a of the open-pore 2, or in such a manner as to get considerably deep into the open-pore 2 when the open-pore 2 has a large diameter. Alternatively, the electrode mixture 3 is supported in such a manner that the electrode mixtures 3 filled in the open-pore 2 from both surfaces of the metal foil 1 come into contact with each other within the open-pore 2.

That is, these open-pores 2 offer an anchoring effect to the electrode mixture 3.

These open-pores 2 are formed randomly, so that not all pores are present as an open-pore penetrating the metal foil 1 from the surface 1a to the surface 1b, and some pores may be closed at an intermediate position.

For this metal foil 1, it is preferable that the thickness thereof be usually 8 to 100 μm in order to obtain a foil with a porous structure. If the metal foil 1 is too thin, it may be broken in the foil manufacturing process, described later. If it is too thick, the aforesaid open-pores are not formed.

It is preferable that the diameter of the opening 2a of the open-pore 2 be within the range of 0.1 to 80 μm , though changing depending on the thickness of the metal foil 1. Also, it is preferable that 1 to 500 pores be distributed per unit area (1 mm^2) on the surface of the metal foil 1.

If the diameter of the open-pore 2 is smaller than 0.1 μm , the electrode mixture 3 does not get into the pore smoothly even if the electrode mixture is applied to and pressed on the metal foil 1, so that the aforementioned anchoring effect is decreased, resulting in a decrease in contact strength between the electrode mixture 3 and the metal foil 1. If the diameter of the open-pore 2 is larger than 80 μm , the mechanical strength of the metal foil 1 decreases, so that the metal foil 1 is broken, for example, when the metal foil 1 is separated from the surface of the moving cathode body in the metal foil manufacturing process, described later.

If the distribution density of these pores on the surfaces 1a and 1b of the metal foil 1 is lower than 1 pore/ mm^2 , the contact strength between the electrode mixture 3 and the metal foil 1 decreases, so that the electrode mixture is liable to peel off.

If the distribution density is higher than 500 pores/ mm^2 , though the contact strength between the electrode mixture 3 and the metal foil 1 increases, the metal foil is too porous as a whole, resulting in a decrease in mechanical strength as described above.

In the electrode manufactured by using the metal foil of the present invention as a collector, the electrode mixture 3 supported on the surfaces 1a and 1b of the metal foil 1 is selected appropriately depending on the battery to be formed.

For example, when the intended electrode is the positive electrode for a nickel-hydrogen battery, the mixture for positive electrode, in which nickel hydroxide powder is used as an active material, is supported on the surfaces of the metal foil. When it is the negative electrode, the mixture for negative electrode, whose principal ingredient is hydrogen occlusion alloy powder, is supported.

When the intended electrode is the positive electrode for a lithium battery, the mixture for positive electrode, whose principal ingredient is an active material such as lithium vanadium pentoxide, lithium manganese oxide, and lithium cobalt oxide, is supported on the surfaces of the metal foil. When it is the negative electrode, the mixture for negative electrode, whose principal ingredient is a powder consisting of C such as chips or powder of pyrolytic carbon, coke, graphite, vitreous carbon, resin baked body, activated charcoal, and carbon fiber, is supported.

The aforementioned metal foil is manufactured continuously as a porous electrolytic metal foil by operating the apparatus described below.

FIG. 3 is a schematic view showing a typical system used when the porous electrolytic metal foil in accordance with the present invention is manufactured. FIG. 4 is a schematic view showing another system.

In FIG. 3, an electrolytic bath 4 contains an electrolyte 5 containing metal ions which are the raw material for an electrolytic metal foil to be manufactured, an anode body 6 is disposed in this electrolyte 5, and a drum cathode body 7 facing the anode body 6 is disposed in such a manner that part of the drum cathode body 7 is immersed in the electrolyte 5.

The anode body 6 is usually made of lead. For the moving cathode body 7, 7', at least the surface thereof is made of stainless steel, Ti, Cr, Al, or Cr-Al alloy.

Electrolytic reaction is carried out by applying electric current to between the anode body 6 and the drum cathode body 7 while the drum cathode body 7 is rotated in the direction indicated by arrow p to move the surface thereof successively in the electrolyte 5 and while the electrolyte 5 is supplied continuously from a distributor 9 to a gap 8 between the anode body 6 and the drum cathode body 7.

In the system shown in FIG. 4, a belt cathode body 7' is used in place of the drum cathode body 7 shown in FIG. 3. This belt cathode body 7' is circulated in the direction indicated by arrow p, by which the surface thereof is moved successively in the electrolyte 5.

In the present invention, the aforementioned drum cathode body 7 and belt cathode body 7' are called a moving cathode body because the surface thereof on which an electrolytic metal foil is formed moves.

The metal ions are electrically deposited on the surface of the drum cathode body 7 or belt cathode body 7', where a metal thin layer is continuously formed so that the layer thickness increases successively in the moving direction of the surface of the drum cathode body 7 or belt cathode body 7'. This metal thin layer is separated from the surface of the drum cathode body 7 or belt cathode body 7' at a point where the surface emerges from the electrolyte, and wound around a take-up roll 11 as the electrolytic metal foil 1 via rolls 10a and 10b.

In the method of the present invention, an exposed surface 7a, 7'a, which is exposed on the drum cathode body 7

or belt cathode body 7' by this separation of the metal thin layer from the surface of the drum cathode body 7 or belt cathode body 7', is subjected to surface treatment, described later.

This surface treatment is carried out to form a film consisting of an electrical insulating material on the exposed surface 7a, 7'a of the moving cathode body 7, 7'.

5 Specifically, the surface treatment includes,

- a treatment for forming an oxide film with a thickness of at least 14 nm on the exposed surface 7a, 7'a by applying electrolytic oxidation to the exposed surface 7a, 7'a (called a first surface treatment);
- 10 a treatment for making stick an organic substance on the exposed surface 7a, 7'a by spraying the organic substance onto the exposed surface 7a, 7' (called a second treatment); and
- a treatment for making stick an organic substance on the exposed surface 7a, 7'a by suspending the organic substance in the electrolyte (called a third treatment).

The following is a detailed description of these surface treatments.

15 First, the first surface treatment will be described. As shown in FIGS. 3 and 4, a oxide film forming apparatus A, described later, is mounted on the exposed surface 7a, 7'a of the moving cathode body 7, 7' from which the metal thin layer is separated. By operating this apparatus A, the exposed surface 7a, 7'a is electrolytically oxidized in the process before the exposed surface 7a, 7'a is immersed again in the electrolyte 5, so that an oxide film with a thickness of at least 14 nm is formed on the whole surface.

20 If the aforesaid metal thin layer is formed on the surface of the drum cathode body 7 or belt cathode body 7' with the oxide film formed on the surface, the metal thin layer is made to have a porous structure having open-pores. When the electrolytic metal foil is formed by separating the metal thin layer from the moving cathode body such as the drum cathode body 7 or belt cathode body 7', both of the surface (S surface) on the moving cathode body side and the opposite surface (M surface) become rough. Moreover, the opposite surface becomes rougher than the surface on the moving cathode body side.

25 At this time, if the formed oxide film is made thinner than 14 nm, the metal thin layer formed on the oxide film is difficult to have a proper porous structure having the aforesaid open-pores and the distribution density thereof. This decreases the performance of metal foil as a collector on which the electrode mixture as described above is supported with a high contact strength.

30 However, if the oxide film is made too thick, the metal thin layer formed on the oxide film becomes excessively porous, by which the mechanical strength thereof is decreased, so that a trouble such that the metal thin layer is broken when it is separated from the moving cathode body occurs frequently. Therefore, it is preferable that the thickness of the oxide film be not greater than 100 nm.

35 The apparatus A for forming the oxide film, which functions in the above-described manner, on the exposed surface of the moving cathode body includes holding means for holding an electrolytic treatment liquid for electrolytic oxidation so that the treatment liquid is in contact with the exposed surface of the moving cathode body; a counter electrode body disposed in the holding means so as to oppose to the exposed surface of the moving cathode body; and supply means for supplying the electrolytic treatment liquid to the holding means.

40 This apparatus A anodizes the exposed surface by applying electric current to between the moving cathode and the counter electrode body with the electrolytic treatment liquid supplied continuously from the supply means to the holding means and with the electrolytic treatment liquid in contact with the exposed surface of the moving cathode body while the metal thin layer is formed on the surface of the moving cathode body by applying electric current to between the anode body and the moving cathode body to continue electrolytic plating, without stopping the operation of the moving cathode body.

45 At this time, the operation is performed so that the operation potential is lower in the order of the anode body, moving cathode body, and counter electrode body. This is because if the operation potential does not establish the above relationship, the exposed surface of the moving cathode body is not electrolytically oxidized, so that the oxide film is not formed there.

The oxide film may be formed continuously or intermittently using the apparatus A.

50 When the metal thin layer formed by electric deposition is separated from the surface of the moving cathode body, part of the oxide film is removed to the metal thin layer side at the same time, so that the thickness of the oxide film is decreased gradually by the repetition of electric deposition and separation. Therefore, the metal thin layer formed on the oxide film does not become to have the proper porous structure as described above. To compensate the decreased thickness, the oxide film must be formed continuously or intermittently.

55 To operate the apparatus A, the constant current method or constant voltage method can be used. Of these two methods, the constant voltage method is preferable because the part of oxide film removed from the surface of the moving cathode body can be compensated automatically and instantly, and the thickness of the oxide film can be prevented from increasing up to the unnecessary thickness.

An example A₁ of the apparatus A will be described with reference to the drawing.

FIG. 5 is a partially cutaway perspective view showing a state in which an apparatus A₁ is mounted on the exposed surface 7a of the drum cathode body 7.

This apparatus A₁, having a shaft 12 for mounting the apparatus at the center, comprises a conductive roll 13 functioning as a counter electrode body opposing to the drum cathode body 7 in electrolytic oxidation, electrolytic treatment liquid holding means 14 disposed around the conductive roll 13, and a pipe which is electrolytic treatment liquid supply means 15 for supplying electrolytic treatment liquid 15a used for electrolytic oxidation to the electrolytic treatment liquid holding means 14. By rotatably supporting the shaft 12 by not-illustrated means with the electrolytic treatment liquid holding means 14 in contact with the exposed surface 7a of the drum cathode body 7 indicated by an imaginary line,

10 the whole of the apparatus A₁ is mounted on the exposed surface 7a of the drum cathode body 7 as shown in FIG. 3.

The conductive roll 13 may be a roll the whole of which is made of a corrosion-resistant material such as titanium, nickel, chromium, copper, and stainless steel or a roll in which the surface of the above material is coated with a material having electric conductivity and resistance to corrosion caused by the electrolytic treatment liquid 15a used to form the oxide film, such as silver, silver alloy, gold, gold alloy, palladium, and palladium alloy. Also, the surface of a roll made of 15 a non-conductive plastic material such as polypropylene or polyvinyl chloride may be covered with foil, wire, or mesh of a material having electric conductivity and corrosion resistance. Alternatively, a material having electric conductivity and corrosion resistance may be plated, thermally sprayed, or applied to the surface of the aforementioned roll. To sum up, a roll at least the surface of which has electric conductivity and corrosion resistance is used as a counter electrode body for electrolytic oxidation on the surface of the drum cathode body.

20 The electrolytic treatment liquid holding means 14 surrounding the conductive roll (counter electrode body) 13 has a proper elasticity as well as permeability. The electrolytic treatment liquid holding means 14 is formed by covering the outer periphery of the conductive roll 13 with a material having resistance to corrosion caused by the electrolytic treatment liquid used, such as felt, nonwoven fabric cloth, or split yarn of polyurethane, polyvinyl formal, or polyester.

Above the electrolytic treatment liquid holding means 14, the pipe 15 formed with a plurality of openings 15b in the 25 axial direction of the electrolytic treatment liquid holding means 14 is disposed as electrolytic treatment liquid supply means, and the predetermined electrolytic treatment liquid 15a is supplied to the pipe 15 by means of a pump 15c. The supplied electrolytic treatment liquid 15a is not subject to any special restriction, and a liquid which does not have an adverse effect on the manufacture of metal thin layer even if being mixed with the electrolyte used for the manufacture 30 of metal thin layer is used. For example, a liquid which is the same as the electrolyte used at present to make metal electrically deposit on the surface of the drum cathode body, or a liquid which has the same components as those of the electrolyte but a different ratio of components can be used.

As the electrolyte, for example, copper sulfate solution is used in manufacturing electrolytic copper foil, and nickel sulfate solution or nickel sulfamate solution is used in manufacturing electrolytic nickel foil. Also, in manufacturing electrolytic aluminum foil, AlCl₃-LiAlH₄-tetrahydrofuran bath and NaF • 2Al(C₂H₅O)₃ • 4 toluene bath, which are disclosed 35 in Japanese Patent Publication No. 48-4460, and the like can be used.

As the electrolytic treatment liquid 15a, a liquid which does not contain ions of metal deposited on the drum cathode body 7 can also be used. Such electrolytic treatment solutions include an acidic solution such as sulfuric acid solution, phosphoric acid solution, and hydrochloric acid solution and a neutral solution in which sodium sulfate, potassium sulfate, sodium hydrochloride, potassium hydrochloride, etc. are dissolved. Among these, sulfuric acid solution is preferably used in manufacturing electrolytic copper foil by using copper sulfate electrolyte.

The supply means for the electrolytic treatment liquid 15a is not limited to the above-mentioned pipe-form means. For example, the conductive roll 13 is made hollow, many openings are formed on the peripheral surface thereof, and the electrolytic treatment liquid 15a is supplied to the hollow portion of the conductive roll 13, by which the electrolytic treatment liquid 15a may be supplied to the electrolytic treatment liquid holding means 14 from the inside thereof 45 through the openings on the peripheral surface of the conductive roll 13.

When the apparatus A₁ is used, the oxide film is formed on the exposed surface 7a of the drum cathode body 7 in the following manner.

First, the electrolytic treatment liquid holding means 14 of the apparatus A₁ is elastically brought into contact with the exposed surface 7a of the drum cathode body 7 rotating in the direction indicated by arrow p. Thereupon, the electrolytic treatment liquid holding means 14 rotates automatically in the direction indicated by arrow r in FIG. 5. With this state being kept, a predetermined electrolytic treatment liquid 15a is supplied to the pipe (electrolytic treatment liquid supply means) 15.

The electrolytic treatment liquid 15a drips onto the electrolytic treatment liquid holding means 14 from the openings 15b, permeates into the electrolytic treatment liquid holding means 14, and is kept therein. As a result, the conductive roll (counter electrode body for electrolytic oxidation) 13 and the exposed surface 7a of the drum cathode body 7 becomes conductive via the electrolytic treatment liquid 15a.

Then, terminals 13a, 13a attached to the conductive roll 13 are connected to the minus side of a power supply (not shown), and the exposed surface 7a of the drum cathode body 7 is connected to the plus side of the power supply so

that an electrolytic current flows between the conductive roll 13 and the exposed surface 7a of the drum cathode body 7, whereby the exposed surface is anodized. At this time, the conductive roll (counter electrode body) 13 is operated so that the potential becomes to be lower than the potential of the drum cathode body in the electrolytic bath on which surface is formed a metal thin layer, and at the same time, the potential of the anode body positioned in the electrolytic bath is made higher than that of the drum cathode body. If the potential of the drum cathode body is higher than that of the anode body, there occurs a trouble such that metal is not electrically deposited on the surface of the drum cathode body, or a trouble such that if electric current is applied so that the potential of the conductive roll is higher than that of the drum cathode body, the conductive roll 13 is made the plus electrode, and the exposed surface 7a of the drum cathode body 7 is made the minus electrode, so that the exposed surface 7a of the drum cathode body 7 is not electrolytically oxidized.

By properly selecting the rotational speed of the drum cathode body 7, the operation potential of the conductive roll (counter electrode body), and the like, an oxide film with a desirable thickness is formed on the exposed surface 7a.

In this apparatus A₁, it is preferable that the width of the electrolytic treatment liquid holding means 14 is smaller than that of the drum cathode body 7 so that both side portions 7b, 7b on the exposed surface 7a of the drum cathode body 7 are not electrolytically oxidized.

The reason for this is as follows: The metal thin layer directly formed at these portions 7b, 7b has a higher mechanical strength than the porous metal thin layer formed on the oxide film produced by the apparatus A₁. Therefore, when the metal thin layer is separated from the drum cathode body, a trouble of breaking of the metal thin layer in the process of separation can be prevented by starting the separation from the portion of metal thin layer formed at the portions 7b, 7b.

FIG. 6 is a partially cutaway perspective view showing a state in which another apparatus A₂ is mounted on the exposed surface 7a of the drum cathode body 7.

In the case of this apparatus A₂, the electrolytic treatment liquid holding means 16 is a box-shaped vessel whose one face is open, and this opening 16a is disposed in liquid-tight slidable contact with or close to the exposed surface 7a of the drum cathode body 7. Therefore, the portions of sides 16b, 16b of the vessel 16, which are in slidable contact with or close to the exposed surface 7a of the drum cathode body 7, are curved so as to match the curvature of the exposed surface 7a of the drum cathode body 7.

The width of the vessel 16 is smaller than that of the drum cathode body 7 for the same reason as that in the case of the electrolytic treatment liquid holding means 14 for the apparatus A₁, so that both side portions 7b, 7b of the exposed surface 7a of the drum cathode body 7 are not electrolytically oxidized.

It is preferable that the vessel 16 be made of a material which is resistant to corrosion caused by the electrolytic treatment liquid used, such as polyvinyl chloride and polypropylene.

In the case where the vessel 16 is disposed so as to be in slidable contact with the exposed surface 7a of the drum cathode body 7, it is preferable that the vessel 16 be made of a material having wear-resistance, lubricity, and elasticity, such as polyethylene, polyester, polyurethane, and silicone rubber. In this vessel 16, a counter electrode body 17 for electrolytic oxidation, which is made of, for example, titanium or stainless steel, is disposed. This counter electrode body 17 faces the exposed surface 7a of the drum cathode body 7 exposed to the interior of the vessel 16 through the opening 16a of the vessel 16.

A supply pipe 18a for electrolytic treatment liquid is attached to the side wall of the vessel 16, and a discharge pipe 18b for electrolytic treatment liquid is attached to the top wall thereof, these pipes constituting electrolytic treatment liquid supply means 18. The electrolytic treatment liquid used to form an oxide film is supplied into the vessel 16 through the supply pipe 18a to fill the vessel 16, covers the exposed surface 7a of the drum cathode body 7, and flows out of the system through the discharge pipe 18b.

Electric current is applied to between the counter electrode body 17 and the drum cathode body 7 while allowing the electrolytic treatment liquid to flow in the vessel 16, by which the exposed surface 7a of the drum cathode body which is exposed to the interior of the vessel 16 through the opening 16a can be electrolytically oxidized.

If the vessel 16 is mounted so that some clearance is formed between the opening 16a of the vessel 16 and the exposed surface 7a of the drum cathode body 7, part of the supplied electrolytic treatment liquid flows out along the exposed surface 7a of the drum cathode body 7 through the clearance, so that an electrolytic treatment liquid film with a uniform thickness is formed on the exposed surface 7a of the drum cathode body which is exposed to the interior of the vessel 16 through the opening 16a, by which the forming condition of oxide film is preferably stabilized.

For the electrolytic treatment liquid supplied into the vessel 16, the electrolyte used for manufacturing a metal thin layer is usually used as it is by being pumped up.

FIG. 7 and FIG. 8, which is a sectional view taken along the line VIII-VIII of FIG. 7, are views showing a state in which another apparatus A₃ is mounted on the exposed surface of the drum cathode body.

This apparatus A₃ has electrolytic treatment liquid holding means consisting of a trough-shaped vessel 19. For this trough-shaped vessel 19, the upper part is open, and both of the ends 19a, 19a in the lengthwise direction are sealed. One end 19a is provided with a supply pipe 20 for electrolytic treatment liquid, constituting electrolytic treatment liquid

supply means. On side 19b of the trough-shaped vessel 19 is lower in height than the other side 19c.

The length of the trough-shaped vessel 19 is shorter than the width of the drum cathode body 7 for the same reason as that in the case of the electrolytic treatment holding means 15 of the apparatus A₁ so that both side portions 7b, 7b of the exposed surface 7a of the drum cathode body 7 are not electrolytically oxidized.

5 The trough-shaped vessel 19 is mounted so that the lengthwise direction thereof agrees with the width direction of the drum cathode body 7, and the one side 19b is close to the exposed surface 7a of the drum cathode body so as to form some clearance between the side 19b and the exposed surface 7a of the drum cathode body.

A counter electrode body 17 is disposed on the other side 19c of the trough-shaped vessel 19, and a metal powder removing filter 21 is interposed between the counter electrode body 17 and the exposed surface 7a of the drum cathode body. As a result, the interior of the trough-shaped vessel 19 is divided into a space 19d where the counter electrode body 17 is disposed and a space 19e positioned on the side of the exposed surface 7a of the drum cathode body.

10 The metal powder removing filter 21 prevents metal powder from depositing on the exposed surface 7a of the drum cathode body 7, the metal powder being deposited on the exposed surface 7a of the drum cathode body 7 by a process in which the metal contained in the electrolytic treatment liquid is electrically deposited abnormally as metal powder on the surface of the counter electrode body 17 in the electrolytic treatment, and the metal powder is removed from the counter electrode body by the flow of electrolytic treatment liquid.

15 The electrolytic treatment liquid supplied to the trough-shaped vessel 19 through the supply pipe 20 overflows over the side 19b after filling the trough-shaped vessel 19, and flows down along the exposed surface 7a of the drum cathode body rotating in the direction indicated by arrow p. In this process, therefore, an electrolytic treatment liquid film with a uniform thickness is continuously formed on the exposed surface 7a of the drum cathode body.

20 For the electrolytic treatment liquid, the electrolyte used for manufacturing a metal thin layer may be used as it is. Alternatively, electrolytic treatment liquid supply pipes connecting with the spaces 19d and 19e formed in the trough-shaped vessel 19 may be disposed separately so that, for example, the electrolyte used for manufacturing a metal thin layer is supplied to the space 19d and an electrolyte with a different composition or containing no metal ions is supplied to the space 19e.

25 The cross-sectional shape of the trough-shaped vessel 19 is not limited to a triangular one as shown in FIGS. 7 and 8. The shape may be a polygon such as quadrangle and hexagon or a semicircle. In effect, the trough-shaped vessel 19 may be shaped so that the electrolytic treatment liquid filling the vessel 19 overflows over the side 19b so that a liquid film can be formed on the exposed surface 7a of the drum cathode body.

30 FIG. 9 and FIG. 10, which is a sectional view taken along the line X-X of FIG. 9, are views showing a state in which still another apparatus A₄ is mounted on the exposed surface of the drum cathode body.

This apparatus A₄ has electrolytic treatment liquid holding means 22 consisting of an elongated closed vessel of a convex lens shape in cross section.

35 Specifically, an attaching portion 22b of a counter electrode body 17 for electrolytic oxidation is mounted at the back of a curved plate 22a in a liquid tight manner, both ends 22C, 22C in the lengthwise direction are sealed, a supply pipe 23 for electrolytic treatment liquid is attached to a substantially central position of vessel, and electrolytic treatment liquid spraying means 22d is formed at the tip end of the curved plate 22a, by which the electrolytic treatment liquid supply means for supplying electrolytic treatment liquid onto the exposed surface 7a of the drum cathode body 7 is formed. The spraying means 22d may consist of, for example, a plurality of holes formed along the lengthwise direction of the curved plate 22a or a slit with a predetermined width formed in the lengthwise direction of the curved plate 22a.

40 The length of the closed vessel 22 is shorter than the width of the drum cathode body 7 for the same reason as that in the case of the electrolytic treatment holding means 15 of the apparatus A₁ so that both side portions 7b, 7b of the exposed surface 7a of the drum cathode body 7 are not electrolytically oxidized.

45 The whole vessel is so configured that the counter electrode body 17 is disposed at the attaching portion 22b, the lengthwise direction of the vessel agrees with the width direction of the drum cathode body 7, and spraying means 22d formed in the curved plate 22a is disposed so as to face the exposed surface 7a of the drum cathode body 7 with a predetermined gap.

50 The electrolytic treatment liquid fed into the vessel 22 through the supply pipe 23 by pumping etc. is sprayed from the spraying means 22d after filling the vessel 22 to hit the exposed surface 7a of the drum cathode body 7 rotating in the direction indicated by arrow p, and flows down along the exposed surface 7a, whereby a liquid film with a uniform thickness is formed.

As the electrolytic treatment liquid, the electrolyte used for manufacturing a metal thin layer may be used, and if necessary, another electrolyte such as dilute sulfuric acid solution may be used.

55 While this state is maintained, a predetermined voltage is applied to between an anode of the drum cathode body 7 and a cathode of the counter electrode body 17, by which the exposed surface 7a of the drum cathode body is electrolytically oxidized. Since the drum cathode body 7 is rotated in the direction indicated by arrow p in the figures, an oxide film is formed continuously or intermittently on the exposed surface 7a.

Although in this apparatus A₄, the surface opposing to the exposed surface 7a of the drum cathode body is curved,

the shape is not limited to this one, and any shape such that the electrolytic treatment liquid filling the vessel interior can be sprayed toward the exposed surface 7a of the drum cathode body may be used. Also, means for uniformly distributing the electrolytic treatment liquid, for example, means in which uniform small holes are formed in a pipe and the electrolytic treatment liquid supplied to this pipe is sprayed from these small holes may be provided within the vessel 22. Further, the supply pipe 23 is not necessarily attached to the central position of the apparatus A₄, but may be attached to any position where the electrolytic treatment liquid can be sprayed uniformly from the spraying means 22d.

Also, a metal powder removing filter may be provided between the counter electrode body 17 and the spraying means 22d as in the case of the apparatus A₃ so as to prevent the metal powder electrically deposited on the counter electrode body from flowing out onto the exposed surface 7a of the drum cathode body 7.

This apparatus A₄ achieves an effect that when the electrolyte for manufacturing a metal thin layer, which has a relatively high metal concentration, is used as the electrolytic treatment liquid, the amount of electrolyte used can be decreased by making the spray opening of the spraying means 22d smallest possible, and the deposition of metal salt in the electrolytic treatment liquid used can be inhibited to the utmost by decreasing the amount of scattered electrolyte.

For example, when an electrolytic copper foil is manufactured by using copper sulfate electrolyte, copper sulfate solution having a relatively high copper concentration is used as an electrolyte. When this electrolyte is used as an electrolytic treatment liquid for forming an oxide film, copper sulfate crystals are produced if the temperature is low, and stick to the apparatus and the electrolytic copper foil, thereby inhibiting the smooth operation of the apparatus. In the apparatus A₄ shown in FIGS. 9 and 10, this trouble can be eliminated easily by merely changing the shape of the spraying means 22d and the distance from the spraying means 22d to the exposed surface 7a of the drum cathode body.

Next, a second surface treatment will be described.

In this treatment, by spraying an organic substance onto the exposed surface of moving cathode body, the exposed surface is partially covered with a film formed by the organic substance sticking onto the exposed surface in a speck form.

Specifically, a resin liquid of any kind is sprayed onto the exposed surface of moving cathode body, and then the resin is cured. The sprayed resin liquid turns to minute liquid drops and sticks onto the exposed surface of moving cathode body in a speck form, and is cured on the exposed surface. As a result, a film consisting of hardened particles of the liquid drops is formed on the exposed surface of moving cathode body.

The film formed at this time is not a dense resin film of the resin constituting the resin liquid used, but is formed by the hardened particles of the resin sticking discontinuously onto the exposed surface of moving cathode body.

Therefore, when electric current is applied to between the moving cathode body and the anode body to carry out electrolytic reaction, electric deposition is inhibited at the portions of the hardened particles, so that the metal thin layer formed on this film becomes porous.

The organic substance used for forming this film is not subject to any special restriction, and may be any organic substance which is electrically insulating and capable of being sprayed. A resin liquid in which a resin such as polyester, epoxy resin, polyamide, and polyurethane is dissolved in an appropriate solvent can be used.

Also, by appropriately selecting the spraying conditions such as spraying pressure, diameter of nozzle used for spraying, and discharge amount of resin liquid, the size and distribution density of the hardened particles are changed, whereby the porosity of this film, and in turn, the porosity of metal thin layer formed on the film can be regulated.

In a third surface treatment, an organic substance is suspended in the electrolyte.

In the apparatuses shown in FIGS. 3 and 4, the anode body 6 is usually formed of a material insoluble in electrolyte, such as lead, so that a large quantity of oxygen gas is generated from the surface of the anode body 6 when electric current is applied, and heavily agitates the electrolyte flowing between the anode body 6 and the moving cathode body 7, 7'. Therefore, if an organic substance is added to the electrolyte in the course of electrolytic plating, the organic substance is dispersed and suspended in a particulate form in the electrolyte being agitated.

The organic substance used in this treatment may be any organic substance which is electrically insulating, insoluble in electrolyte, and suspended in a particulate state in electrolyte. For example, various machine oils or insulating oils are used.

In this treatment, when the moving cathode body is moved and immersed in the electrolyte, the aforesaid organic substance, which is dispersed and suspended in a particulate state in the electrolyte, sticks onto the exposed surface.

As a result, particulates of organic substance are formed in a row on the exposed surface of moving cathode body, so that a microscopically porous film is formed.

Since electric current is applied to between the moving cathode body and the anode body in this process, the metal thin layer formed on this film also becomes porous for the same reason as described regarding the second surface treatment.

At this time, by appropriately selecting the kind of the suspended organic substance, suspension concentration, and the like, the porosity of film, and in turn, the porosity of metal thin layer formed on the film can be regulated.

On the surface of metal foil thus manufactured, a preservative film may be formed, if necessary, for actual use by using an organic preservative such as benzotriazole or an inorganic preservative such as chromate treatment liquid.

Also, if, for example, a silane coupling agent is applied onto the surface of manufactured metal foil, the contact strength between the electrode mixture and the metal foil can be enhanced when the electrode mixture is supported on the surface of metal foil.

5 BRIEF DESCRIPTION OF THE DRAWINGS

- FIG. 1 is a sectional view showing a typical cross-sectional structure of a metal foil manufactured by a method in accordance with the present invention;
- 10 FIG. 2 is a sectional view of a typical electrode with a collector using a metal foil manufactured by a method in accordance with the present invention;
- FIG. 3 is a schematic view showing a manufacturing system for an electrolytic metal foil;
- 15 FIG. 4 is a schematic view showing another manufacturing system;
- FIG. 5 is a partially cutaway perspective view showing a state in which an apparatus A_1 used for forming an oxide film is mounted on the exposed surface of a drum cathode body;
- FIG. 6 is a partially cutaway perspective view showing a state in which an apparatus A_2 used for forming an oxide film is mounted on the exposed surface of a drum cathode body;
- 20 FIG. 7 is a partially cutaway perspective view showing a state in which an apparatus A_3 used for forming an oxide film is mounted on the exposed surface of a drum cathode body;
- FIG. 8 is a sectional view taken along the line VIII-VIII of FIG. 7;
- 25 FIG. 9 is a partially cutaway perspective view showing a state in which an apparatus A_4 used for forming an oxide film is mounted on the exposed surface of a drum cathode body; and
- FIG. 10 is a sectional view taken along the line X-X of FIG. 9.

BEST MODE OF CARRYING OUT THE INVENTION

25 Working examples 1 and 2, comparative examples 1 and 2 1) Manufacture of metal foil

In the system shown in FIG. 3, the drum cathode body 7 was made of titanium, and the apparatus A_4 shown in FIGS. 9 and 10 was mounted on the surface of the drum cathode body 7.

30 The electrolyte 5 with a copper ion concentration of 100 g/liter, a sulfuric acid concentration of 100 g/liter, and a bath temperature of 60°C was supplied into the electrolytic bath 4. While the drum cathode body 7 was rotated, an electric current with a current density of 60 A/dm² was applied to between the drum cathode body 7 and the anode body 6 to continuously form a copper thin layer on the surface of the drum cathode body 7. By separating the copper thin layer from the surface of the drum cathode body 7, the electrolytic copper foil 1 was manufactured continuously.

35 While the manufacture of the electrolytic copper foil 1 was continued, the aforesaid electrolyte was supplied into the closed vessel 22 through the supply pipe 23 of the apparatus A_4 , and sprayed onto the exposed surface 7a of the drum cathode body 7 rotating in the direction indicated by arrow p from the spraying means 22d while the voltage between the drum cathode body 7 and the counter electrode body (made of titanium) 17 was kept at a constant value of 50 V.

40 A titanium oxide film with a thickness of 70 nm was formed continuously on the exposed surface 7a of the drum cathode body 7.

Copper was electrically deposited on this titanium oxide film to form a copper thin layer. By continuously separating the copper thin layer from the drum cathode body 7, the electrolytic copper foil 1 was obtained.

45 Then, the obtained electrolytic copper foil 1 was subjected to surface roughening with a current density of 30 A/dm² by using an electrolyte with a copper ion concentration of 20 g/liter, a sulfuric acid concentration of 40 g/liter, and a bath temperature of 30°C.

For the electrolytic copper foil after surface roughening, the average thickness was 50 µm, and the surface roughnesses (Rz) of the separation surface (S surface) from the drum cathode body and the opposite surface (M surface) were 5 µm and 11 µm, respectively.

50 Also, in this electrolytic copper foil, open-pores communicating in the thickness direction were found. The diameter of the open-pore was 0.1 to 3 µm, and the distribution density thereof was 100 to 200 pores/mm².

2) Manufacture of electrode

Ten parts by weight of polyvinylidene fluoride powder was mixed with 100 parts by weight of KETJEN BLACK 55 EC(carbon black manufactured by AKZO CO., LTD., specific surface area: 950 m²/g, average grain size: 0.03 µm), and 30 parts by weight of N-methylpyrrolidone was added to the resultant mixed powder to prepare paste of active material mixture.

This paste was applied to both of the surfaces of the aforesaid electrolytic copper foil, dried, and press-formed at a

pressure of 2000 kg/cm² to manufacture a working example electrode 1 of 100 µm thick, 10 mm wide, and 20 mm long. The amount of active material mixture supported on this electrode was 20 mg.

5 A working example electrode 2 was manufactured in the same way as in the case of the working example electrode 1 except that the electrolytic copper foil was manufactured while forming a titanium oxide film of 14 nm thick on the exposed surface 7a of the drum cathode body 7 by applying a constant voltage of 10 V to between the counter electrode body 17 and the drum cathode body 7 when the oxide film was formed.

For the electrolytic copper foil used for this working example electrode 2, the average thickness was 50 µm, the Rz of S surface was 2 µm, the Rz of M surface was 10 µm, the diameter of open-pore was 0.1 to 3 µm, and the distribution density thereof was 20 to 40 pores/mm².

10 For comparison, a rolled copper foil of 50 µm thick was prepared, and 20 mg of an active material mixture was put on both of the surfaces thereof in the same way as described above to manufacture a comparative example electrode 1.

Also, both of the surfaces of the aforesaid rolled copper foil were roughened to about Rz 2 to 5 µm with #300 emery paper, and 20 mg of an active material mixture was put thereon in the same way as in the working examples to manufacture a comparative example electrode 2.

15

3) Cycle life of electrode

An electrolyte formed by dissolving lithium perchlorate of 1 M in propylene carbonate of 1 kg was prepared. Each of the aforesaid electrodes was disposed in this electrolyte as a negative electrode, and metallic lithium foils were disposed as a counter electrode and a reference electrode, by which four kinds of three-electrode cells were assembled.

20 Then a charging/discharging cycle test was made. In one cycle of this test, a constant current of 1.2 mA was applied to the aforesaid three-electrode cell to perform charging until the voltage reached 0 V with respect to the potential of the reference electrode, the current application was halted for 20 minutes, and then discharging was performed with a constant current of 1.2 mA until the voltage reached 1.5 V with respect to the potential of the reference electrode.

25

For each three-electrode cell, the discharge capacity at the 20th cycle in the charging/discharging cycle test was compared with the discharge capacity at the 1st cycle, and the ratio (%) of the former to the latter was calculated. The result is given in Table 1.

30

Table 1

35

	Ratio of discharge capacity in charging/discharging cycle test (%: 20th cycle/1st cycle)
Working example electrode 1	97 or higher
Working example electrode 2	About 80
Comparative example electrode 1	About 40
Comparative example electrode 2	About 70

40

As is apparent from the above result, the discharge capacity of the working example electrode is less prone to decrease in the process of charging/discharging cycle, so that the working example electrodes have excellent cycle life characteristics.

45

The reason for this is that because the collector (electrolytic copper foil) has a porous structure of the aforesaid specification, the contact strength between the collector and the active material mixture supported on the collector is high, so that the active material mixture is effectively prevented from peeling off in the process of the charging/discharging cycle test. Also, the reason for this is thought to be that because the electrolytic copper foil is porous and open-pores penetrate the foil in the thickness direction, lithium ions pass through the open-pores between the active material mixtures supported on the surfaces, so that a uniform electron transfer reaction proceeds.

Working example 3

55

The apparatus A₃ shown in FIGS. 7 and 8 was mounted on the exposed surface of a titanium-made drum cathode body. An electrolytic copper foil was manufactured while a 35 nm thick titanium oxide film was formed on the exposed surface 7a of the drum cathode body 7 by applying a constant voltage of 25 V to between the counter electrode body 17 and the drum cathode body 7. The resultant electrolytic copper foil was subjected to surface roughening under the same conditions as in the case of the working example electrode 1.

The obtained electrolytic copper foil had a porous structure in which the average thickness was 25 µm, the Rz of S surface was 2 µm, the Rz of M surface was 9 µm, the diameter of open-pore was 0.1 to 3 µm, and the distribution density thereof was 150 to 250 pores/mm².

5 A collector with an average thickness of 50 µm whose surface consisted of the M surface was formed by lapping the electrolytic copper foil over another with their S surfaces being brought into contact with each other, and an active material mixture was put on the M surfaces in the same way as in the case of the working example electrode 1, by which a working example electrode 3 was manufactured.

This electrode was subjected to the same charging/discharging cycle test as in the case of the working example electrode 1.

10 This electrode showed a value of 98% or higher of the ratio of discharge capacity at the 20th cycle to discharge capacity at the 1st cycle, exhibiting excellent cycle life characteristics.

Working example 4

15 The apparatus A₁ shown in FIG. 5 was mounted on the exposed surface of a titanium-made drum cathode body. An electrolytic copper foil was manufactured while a 70 nm thick titanium oxide film was formed on the exposed surface 7a of the drum cathode body 7 by applying a constant voltage of 50 V to between the conductive roll 13 and the drum cathode body 7.

20 The obtained electrolytic copper foil had a porous structure in which the average thickness was 20 µm, the Rz of S surface was 2 µm, the Rz of M surface was 6 µm, the diameter of open-pore was 0.1 to 3 µm, and the distribution density thereof was 350 to 450 pores/mm².

25 After an active material mixture was put on the M surface and S surface of this electrolytic copper foil in such a manner that the ratio of amount of mixture supported on the M surface to that on the S surface is 9:1, the electrolytic copper foil was lapped over another with their S surface sides being brought into contact with each other in the same way as in the case of the working example electrode 3, and the lapped foils were dried and press-formed at a pressure of 2000 kg/cm², by which a working example electrode 4 was manufactured.

This electrode was subjected to the same charging/discharging cycle test as in the case of the working example electrode 1.

30 This electrode showed a value of 99% or higher of the ratio of discharge capacity at the 20th cycle to discharge capacity at the 1st cycle, exhibiting excellent cycle life characteristics.

Working example 5

35 Commercially available lithium carbonate (Li₂CO₃) and basic cobalt carbonate (2CoCO₃ + 3Co(OH)₂) were weighed so that the molar ratio of Li/CO is 1:1, and wet-blended using ethanol with a zirconia-made ball mill. Thereafter, the blended material was heat-treated at a temperature of 900°C for two hours to synthesize LiCoO₂.

40 This LiCoO₂ was ground into powder with an average grain size of 16 µm with the ball mill, and 6 parts by weight of graphite powder with an average grain size of 0.1 µm was blended with 100 parts by weight of this powder. Further, 3.5 parts by weight of polyvinylidene powder was dissolved in 30 parts by weight of N-methylpyrrolidone, and the resultant material was added to the aforesaid mixed powder of LiCoO₂ powder and graphite powder to prepare paste of active material mixture (electrode mixture).

Using this paste and using the electrolytic copper foil shown in the working example electrode 1 as a collector, a working example electrode 5 with the active material mixture of 20 mg was manufactured in the same way as in the case of the working example electrode 1.

45 This electrode was subjected to the same charging/discharging cycle test as in the case of the working example electrode 1.

This electrode showed a value of 98% or higher of the ratio of discharge capacity at the 20th cycle to discharge capacity at the 1st cycle, exhibiting excellent cycle life characteristics.

50 Working example 6

In working example 1, the electrolyte was replaced with an electrolyte for manufacturing electrolytic nickel foil, having a nickel sulfate concentration of 300 g/liter, a boric acid concentration of 40 g/liter, and a bath temperature of 60°C, and this electrolyte was used to form a 70 nm thick titanium oxide film on the exposed surface of drum cathode body by 55 using the apparatus A₄. While forming this titanium oxide film, an electrolytic nickel foil was manufactured with a current density of 30 A/dm².

The obtained electrolytic nickel foil had a porous structure in which the average thickness was 25 µm, the Rz of S surface was 2 µm, the Rz of M surface was 7 µm, the diameter of open-pore was 0.1 to 4 µm, the distribution density

thereof was 300 to 400 pores/mm², and the porosity was 5%.

Hydrogen occlusion alloy powder with a composition of MnNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75} (Mn: misch metal) and a grain size of 30 to 50 µm was prepared. Five parts by weight of 60% fluid dispersion of polytetrafluoroethylene powder and 30 parts by weight of 1.2% carboxymethylcellulose solution were mixed with 100 parts by weight of this alloy powder to prepare paste.

This paste was applied to both of the surfaces of the aforesaid two nickel foils, and one nickel foil was lapped over the other with their S surface sides being brought into contact with each other. After being dried, the lapped foils were press-formed at a pressure of 2000 kg/cm², by which a negative electrode for nickel-hydrogen battery with a thickness of 0.8 mm, a width of 70 mm, and a length of 100 mm was manufactured.

Meanwhile, a publicly known positive electrode with a thickness of 0.8 mm, a width of 70 mm, and a length of 100 mm was prepared. In this positive electrode, nickel hydroxide was used as an active material for positive electrode, and the theoretical discharge capacity was set at a value about 0.7 times of the theoretical discharge capacity of aforesaid negative electrode. Separators of 0.2 mm thick made of nylon were interposed between four positive electrodes and five negative electrodes, and a 6N KOH electrolyte was used to assemble a nickel-hydrogen battery with a rated capacity of 10 Ah.

This battery was subjected to a charging/discharging cycle test, in which one cycle consists of 120% overcharging at 0.5 C and discharging down to a final discharge voltage of 1.0 V at 1.0 C, and the decrease ratio of discharge capacity at 500 cycle time was measured.

For comparison, negative electrodes were manufactured as a comparative example electrode 3 and comparative example electrode 4 by using a punching nickel sheet foil with an opening ratio of 10% and a nickel foam with a porosity of 50% as collectors, respectively, and by putting a mixture on the collector under the same conditions as described above, and nickel-hydrogen batteries were assembled. On these batteries as well, the decrease ratio of discharge capacity at 500 cycle time was measured in the same way as in the working example. The results are given in Table 2.

In addition, the tensile strength and elongation of the collector were measured by the method specified in JIS C6511, and the measured value is given in Table 2. Also, the manufacturing cost of the comparative example electrode, which is calculated when the manufacturing cost of the working example electrode 6 is taken as 1, is given as a relative value in Table 2.

Table 2

	Decrease ratio of discharge capacity (%: after 500 cycles)	Mechanical properties of collector		Manufacturing cost (relative value)
		Tensile strength (kg/mm ²)	Elongation (%)	
Working example electrode 6	15	25	7	1
Comparative example electrode 3	20	15	5	3
Comparative example electrode 4	24	5	1	10

As is apparent from the above result, a battery incorporating an electrode in which a metal foil of the present invention is used as a collector has a low decrease ratio of discharge capacity, and thereby has high cycle life characteristics. Also, the collector has high mechanical properties, so that, for example, breakage or like trouble is not caused even when the collector is contained in the battery by being wound. Because the collector is manufactured by electrolytic plating, it can be mass-produced, so that the manufacturing cost can be reduced, which contributes to the provision of inexpensive electrodes.

Working examples 7 and 8

When the electrolytic copper foil of working example 1 was manufactured, the resin liquid described below was sprayed onto the exposed surface 7a of the drum cathode body 7 under the following conditions.

Composition of resin liquid: RIPOXY R-804B (trade name, a resin manufactured by Showa Highpolymer Co., Ltd.)

96.5 wt%, PERMERIC (trade name, a hardening agent manufactured by Showa Highpolymer Co., Ltd.) 3 wt%,

Hardening Accelerator D (trade name, manufactured by Showa Highpolymer Co., Ltd.) 0.5 wt%

Spraying: Pressure Sprayer No. 7760 (trade name, a pressure-type sprayer manufactured by Furupla Co., Ltd.)

5 After the resin liquid was hardened, electrolytic plating was performed under the same conditions as those in working example 1 to form a copper thin layer on the hardened film. By separating the copper thin layer, an electrolytic copper foil was manufactured.

For the obtained electrolytic copper foil, the average thickness was 10 µm, the Rz of S surface was 1.5 µm, and the Rz of M surface was 2.5 µm. In the thickness direction, open-pores with a diameter of 0.1 to 80 µm were found with a distribution density of 1 to 5 pores/mm² on the surface.

10 Without surface roughening, 20 mg of the electrode mixture of working example 1 was put on both of the surfaces of this electrolytic copper foil to manufacture a working example electrode 7.

Also, in working example 1, an electrolytic copper foil was manufactured by performing electrolytic plating under the same conditions as those in working example 1 except that FBK-RO220 (trade name, a machine oil manufactured by

15 Mitsubishi Oil Co., Ltd.) was suspended with a concentration of 100 g/m³ in electrolyte.

For the obtained electrolytic copper foil, the average thickness was 10 µm, the Rz of S surface was 1.5 µm, and the Rz of M surface was 2.3 µm. In the thickness direction, open-pores with a diameter of 0.1 to 60 µm were found with a distribution density of 1 to 10 pores/mm² on the surface.

20 Without surface roughening, 20 mg of the electrode mixture of working example 1 was put on both of the surfaces of this electrolytic copper foil to manufacture a working example electrode 8.

For comparison, without surface treatment on the exposed surface of the drum cathode body, a copper thin layer was formed directly on the exposed surface under the conditions for electrolytic plating in working example 1, and then separated to manufacture an electrolytic copper foil.

25 For the obtained electrolytic copper foil, the average thickness was 10 µm, the Rz of S surface was 1.5 µm, and the Rz of M surface was 2.5 µm. In the thickness direction, no pores were found.

Without surface roughening, 20 mg of the electrode mixture of working example 1 was put on both of the surfaces of this electrolytic copper foil to manufacture a comparative example electrode 5.

By using these electrodes, the same three-electrode cells as in working example 1 were assembled, and a charging/discharging cycle test was made under the same conditions. The result is given in Table 3.

30

Table 3

	Ratio of discharge capacity in charging/discharging cycle test (%: 20th cycle/1st cycle)
Working example electrode 7	About 80
Working example electrode 8	About 85
Comparative example electrode 5	About 60

35

As is apparent from the above result, since the working example electrodes 7, 8 have a collector (electrolytic copper foil) of a porous structure, the discharge capacity is unlikely to decrease in the process of charging/discharging cycle, so that these electrodes have high cycle life characteristics.

40

INDUSTRIAL APPLICABILITY

The metal foil manufactured by the method in accordance with the present invention has many open-pores formed in the thickness direction.

45 Therefore, when this metal foil is used as a collector for a secondary battery, the openings of these open-pores have an anchoring effect on the electrode mixture supported on the metal foil, so that the contact strength between the electrode mixture and the collector is increased, by which the electrode mixture is prevented from peeling off in the charging/discharging cycle.

Also, when this metal foil is used as a collector for the electrode of lithium battery, the electron transfer reaction in 50 battery operation proceeds smoothly via the open-pores of this metal foil, so that the coefficient of use of active material is increased, by which the cycle life characteristics of battery is improved.

Since this metal foil is manufactured by electrolytic plating, it can be mass-produced, so that the manufacturing cost is decreased, which contributes greatly to the manufacture of inexpensive electrodes.

Claims

1. A method of manufacturing a porous electrolytic metal foil, comprising the steps of:

5 continuously forming a metal thin layer by electrically depositing metal ions on the surface of a moving cathode body by an electrolytic reaction which is carried out by immersing an anode body and the moving cathode body in an electrolyte containing metal ions and by applying electric current to between the anode body and moving cathode body while said moving cathode body is moved; and

10 continuously manufacturing an electrolytic metal foil by continuously separating said metal thin layer from the surface of said moving cathode body while said moving cathode body is moved;
and further comprising the step of:
carrying out surface treatment of the exposed surface of said moving cathode body exposed after said metal thin layer is separated by wholly or partially forming a film consisting of an electrical insulating material on said exposed surface.

15 2. A method of manufacturing a porous electrolytic metal foil according to claim 1, wherein said surface treatment is carried out to form an oxide film with a thickness of at least 14 nm by electrolytically oxidizing said exposed surface.

20 3. A method of manufacturing a porous electrolytic metal foil according to claim 1, wherein said surface treatment is carried out to make an organic substance stick to said exposed surface by spraying said organic substance onto said exposed surface.

25 4. A method of manufacturing a porous electrolytic metal foil according to claim 1, wherein said surface treatment is carried out to make an organic substance stick to said exposed surface by suspending said organic substance in said electrolyte.

30 5. A method of manufacturing a porous electrolytic metal foil according to claim 1, wherein said electrolytic metal foil has such a structure that open-pores with a diameter of 0.1 to 80 μm are formed in the thickness direction and the distribution density of said open-pores is 1 to 500 pores/ mm^2 on the surface.

30

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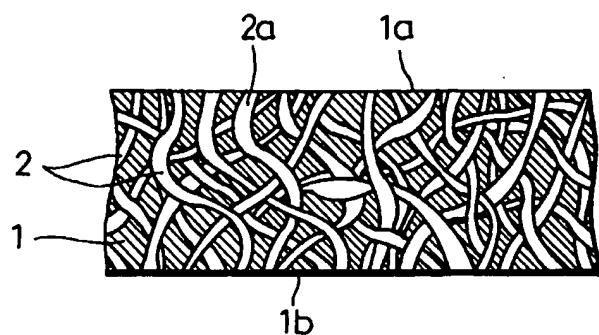
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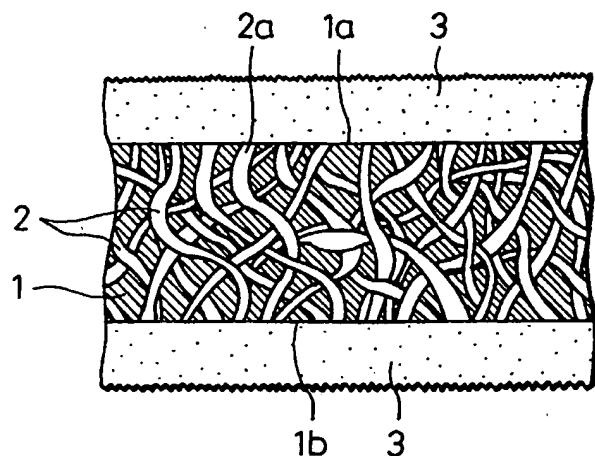
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F I G . 1



F I G . 2



F I G . 3

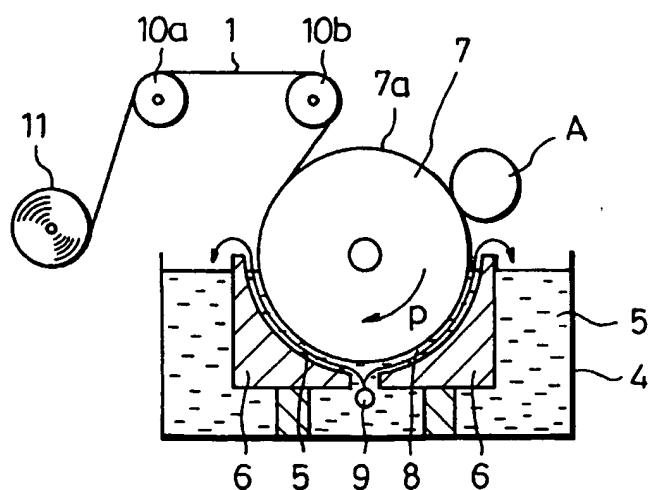
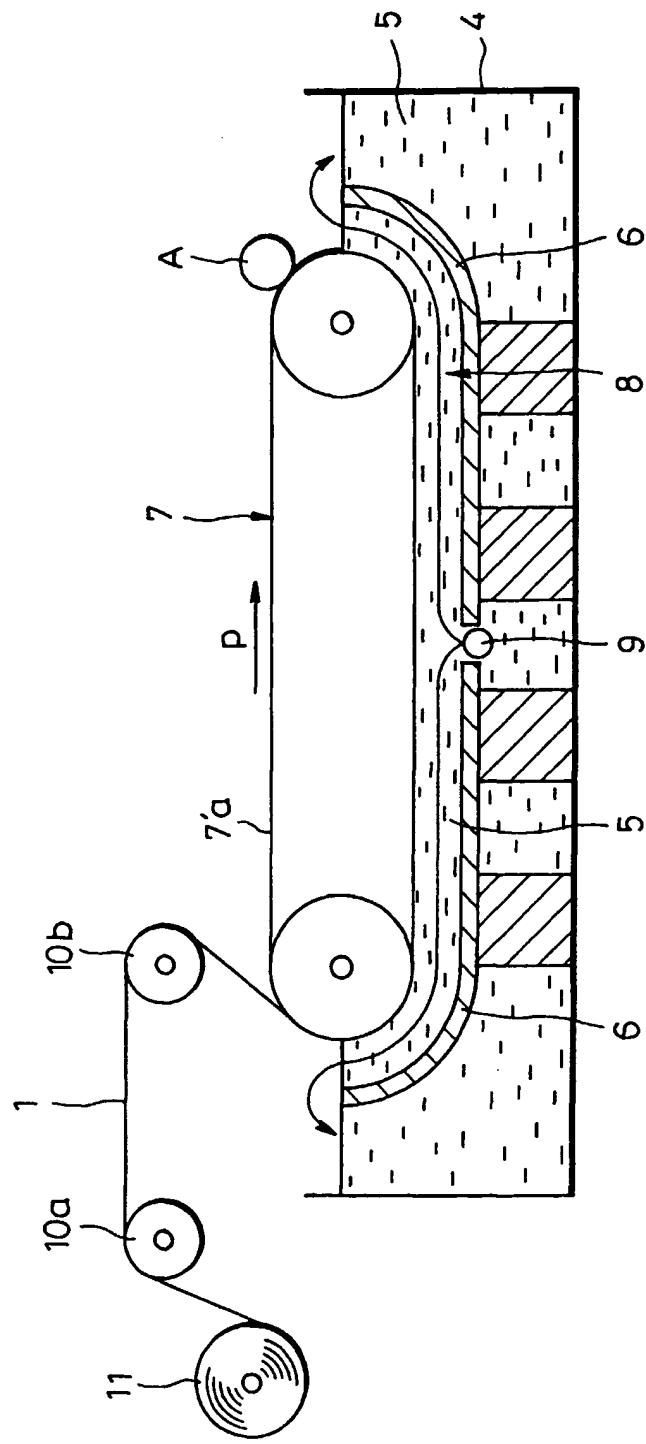


FIG. 4



F I G. 5

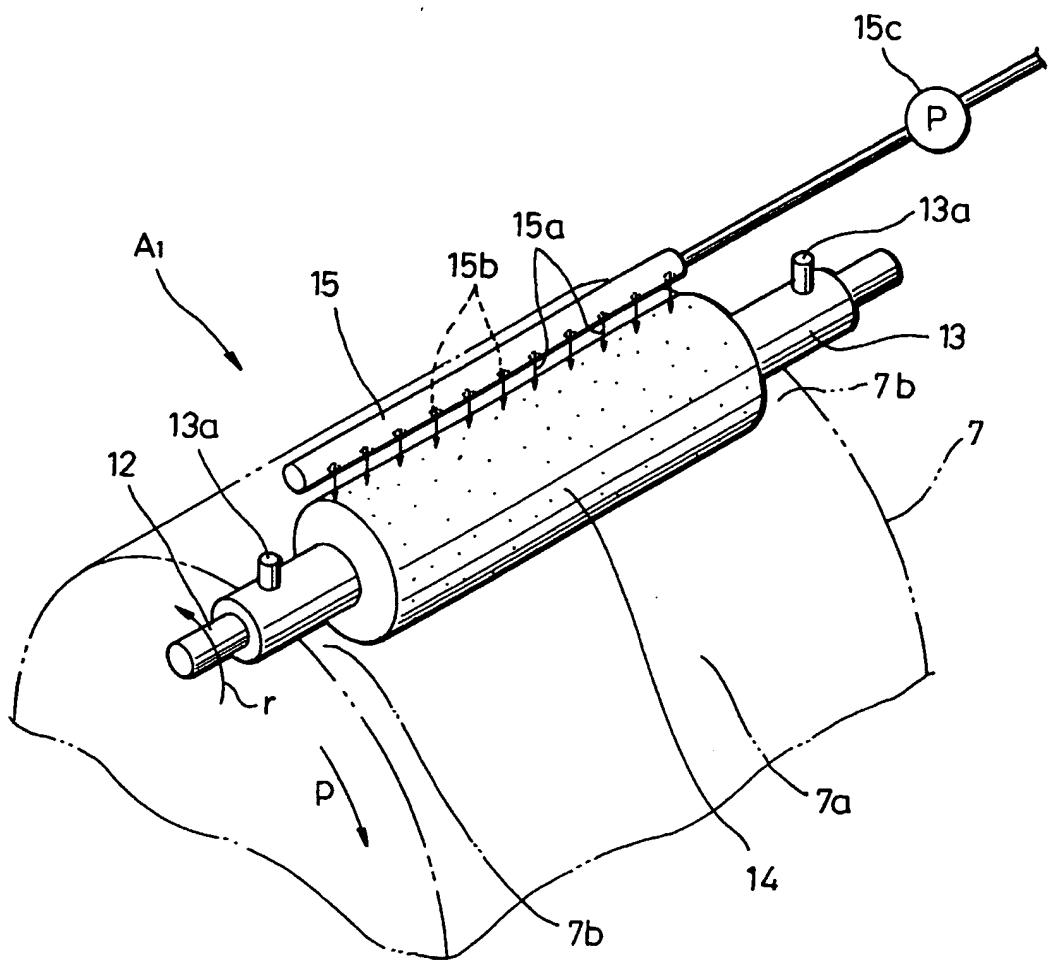


FIG. 6

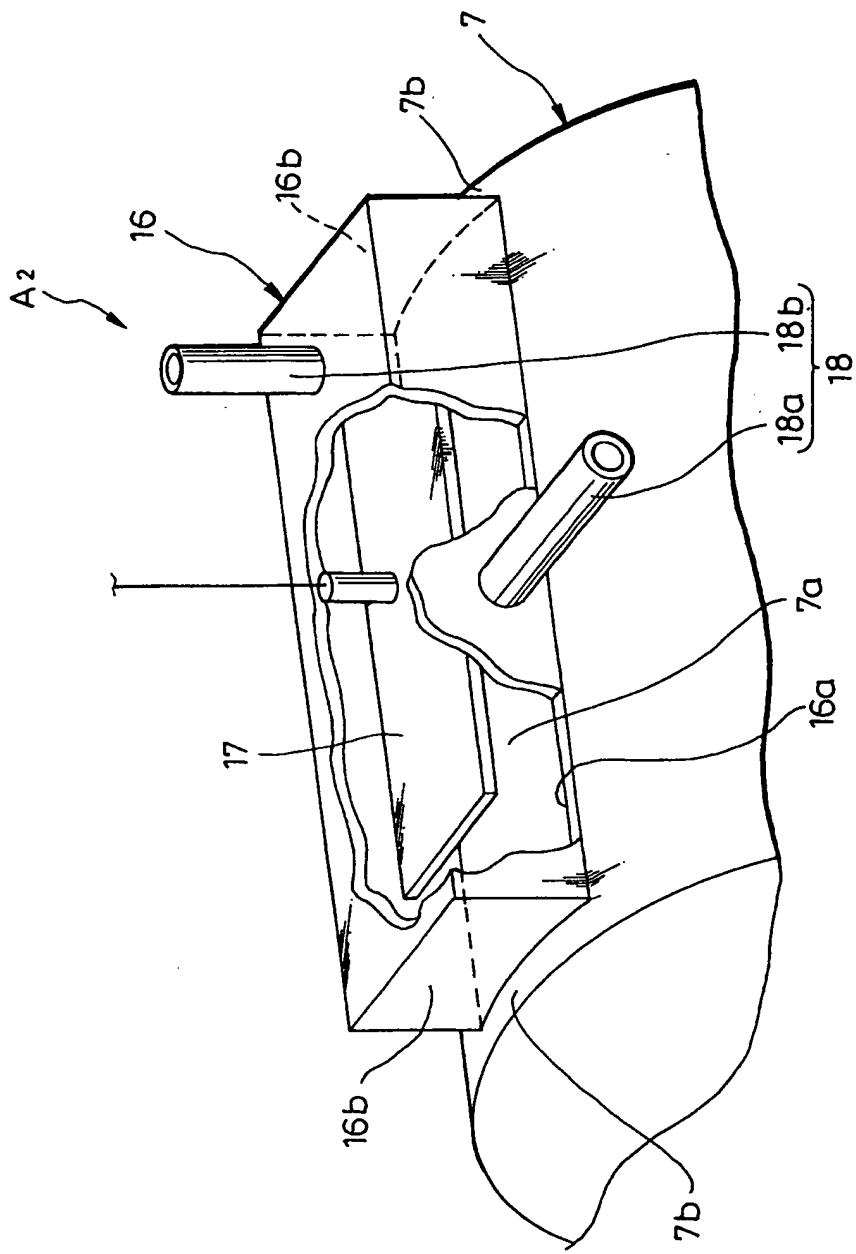


FIG. 7

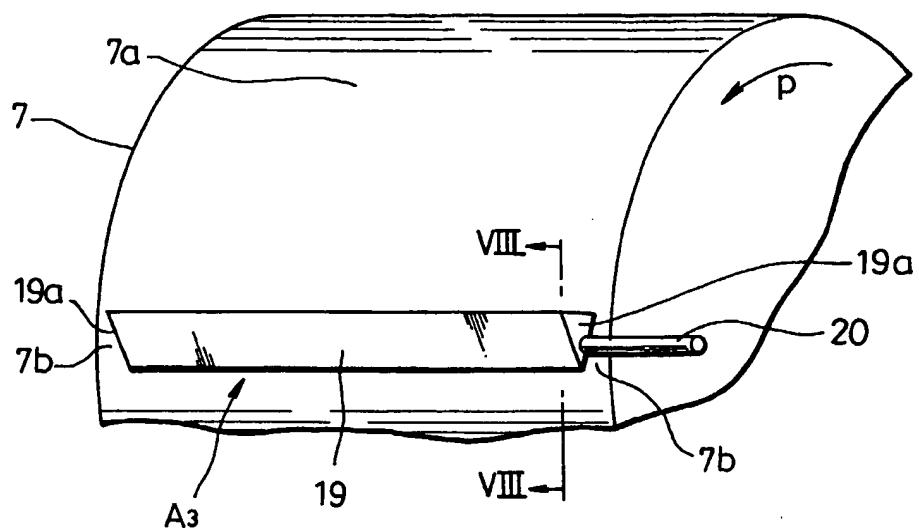


FIG. 8

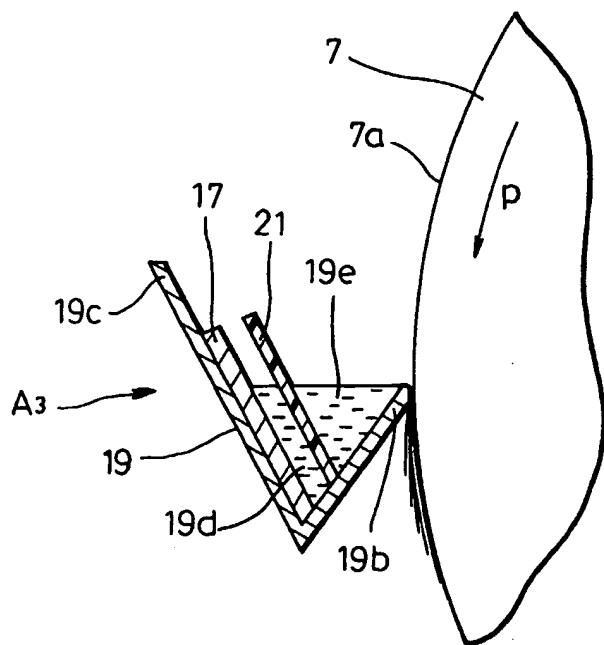
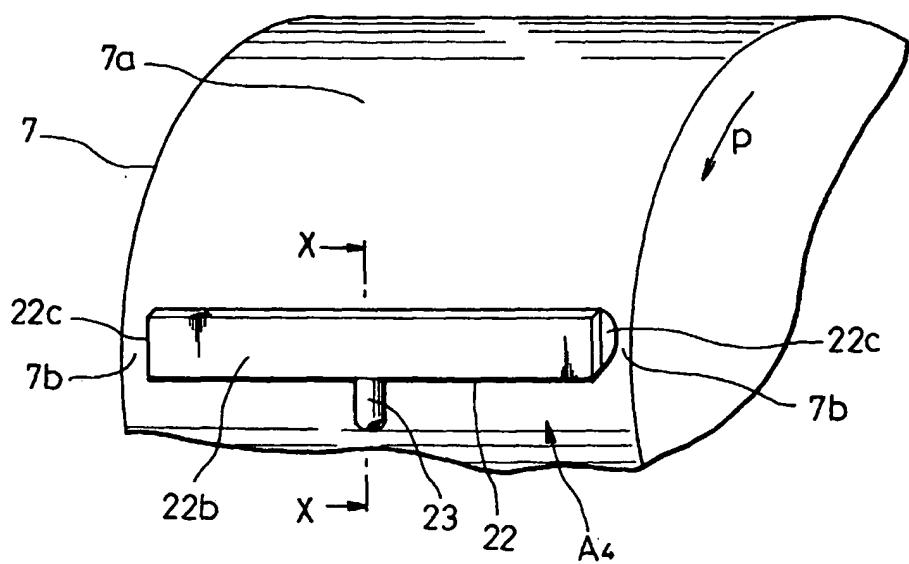
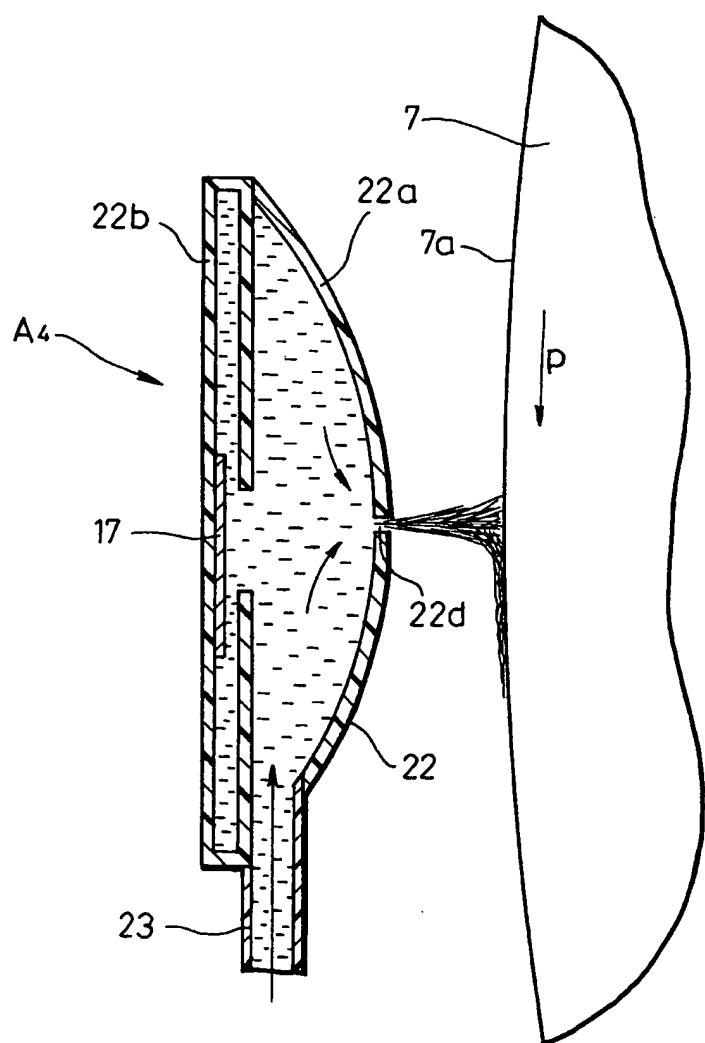


FIG. 9



F I G. 10



INTERNATIONAL SEARCH REPORT		International application No. PCT/JP96/02460						
A. CLASSIFICATION OF SUBJECT MATTER Int. Cl ⁶ C25D1/04, C25D1/08, C25C5/02 According to International Patent Classification (IPC) or to both national classification and IPC								
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int. Cl ⁶ C25D1/04, C25D1/08, C25C5/02								
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926 - 1996 Kokai Jitsuyo Shinan Koho 1971 - 1996 Toroku Jitsuyo Shinan Koho 1994 - 1996								
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)								
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left; padding: 2px;">Category*</th> <th style="text-align: left; padding: 2px;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="text-align: left; padding: 2px;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="padding: 2px;">A</td> <td style="padding: 2px;">JP, 49-79931, A (The Furukawa Electric Co., Ltd.), August 1, 1974 (01. 08. 74) (Family: none)</td> <td style="padding: 2px;">1 - 5</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	A	JP, 49-79931, A (The Furukawa Electric Co., Ltd.), August 1, 1974 (01. 08. 74) (Family: none)	1 - 5
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A	JP, 49-79931, A (The Furukawa Electric Co., Ltd.), August 1, 1974 (01. 08. 74) (Family: none)	1 - 5						
<input type="checkbox"/> Further documents are listed in the continuation of Box C.		<input type="checkbox"/> See patent family annex.						
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(54) PROCESS FOR PREPARING POROUS ELECTROLYTIC METAL FOIL

VERFAHREN ZUR HERSTELLUNG PORÖSER ELKTROLYTISCHER METALLFOLIEN

PROCEDE DE PRODUCTION D'UNE FEUILLE DE METAL ELECTROLYTIQUE POREUSE

(84) Designated Contracting States:
DE FR GB LU

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(56) References cited:
JP-A- 49 079 931 SU-A- 572 538
US-A- 4 073 699 US-A- 5 441 627

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- PATENT ABSTRACTS OF JAPAN vol. 012, no.
059 (C-478), 23 February 1988 (1988-02-23) & JP
62 205296 A (HITACHI CABLE LTD), 9 September
1987 (1987-09-09) -& DATABASE WPI Derwent
Publications Ltd., London, GB; XP002140673
- PATENT ABSTRACTS OF JAPAN vol. 018, no.
647 (C-1283), 8 December 1994 (1994-12-08) & JP
06 248488 A (DENKI KAGAKU KOGYO KK), 6
September 1994 (1994-09-06) -& DATABASE WPI
Derwent Publications Ltd., London, GB;
XP002140674

EP 0 860 518 B1

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Description**TECHNICAL FIELD**

- 5 [0001] The present invention relates to a method of manufacturing a porous electrolytic metal foil and, more particularly, to a method of manufacturing a porous electrolytic metal foil in which when the metal foil is used as a collector of secondary battery, a mixture for electrode can be supported firmly on the collector, and electron transfer reaction can be caused uniformly at the charging/discharging cycle time.

10 BACKGROUND ART

[0002] In recent years, as portable electronic equipment such as video cameras and notebook type computers has widely been used, the demand for small high-capacity secondary batteries has increased as power sources therefor. Most of the secondary batteries now being used are nickel-cadmium batteries containing alkali electrolyte, the battery voltage thereof being about 1.2 V. For this reason, a nickel-hydrogen battery has received attention as a higher-power battery, and also a lithium battery has been developed.

[0003] The nickel-hydrogen battery works with hydrogen used as an active material for negative electrode. The negative electrode thereof is formed by supporting a hydrogen occlusion alloy capable of reversibly occluding/discharging hydrogen on the collector, and the positive electrode is formed by similarly supporting, for example, nickel hydroxide, which is an active material for positive electrode, on the collector.

[0004] For example, when a negative electrode of nickel-hydrogen battery is manufactured, predetermined amounts of hydrogen occlusion alloy powder, conductive material powder such as nickel, and binder powder such as polyvinylidene fluoride are mixed to yield a mixed powder, to which, for example, carboxymethyl cellulose solution is added, by which a slurry, which is a mixture for negative electrode, is prepared. A collector such as a punching Ni sheet with a desirable opening ratio, a Ni foam sheet with a desirable porosity, or a Ni powder sintered body is filled with the slurry. The mixture is supported on the surface of the collector and in the inside voids thereof in a contacting state by sequentially performing drying, rolling, and heat treatment.

[0005] When a positive electrode is manufactured, predetermined amounts of nickel hydroxide powder, which is an active material for positive electrode, and a conductive material such as nickel powder are mixed to yield a mixed powder, to which, a predetermined amount of, for example, carboxymethyl cellulose solution is added, and the whole mixture is agitated into a slurry form, by which a mixture for positive electrode is prepared. Thereafter, a collector such as a Ni foam sheet is filled with the mixture for positive electrode. The mixture for positive electrode is supported on the collector by sequentially drying and rolling it.

[0006] Lithium batteries are broadly classified into metallic lithium batteries and lithium ion batteries.

[0007] For the metallic lithium battery, the negative electrode is formed of metallic lithium, and the positive electrode is formed by supporting an active material for positive electrode such as LiCoO₂ on a collector. For the lithium ion battery, the positive electrode is formed in the same manner as described above, but the negative electrode is formed by supporting, for example, carbon (C) capable of occluding/discharging lithium ions on a collector.

[0008] In the case of the former battery of the batteries of the two types, dendrite recrystallized lithium is deposited on the surface of metallic lithium, which is the negative electrode, during charging, and it grows as the charging/discharging cycle proceeds, so that the battery cycle life is decreased. In the worst case, the grown recrystallized lithium breaks a separator interposed between the positive and negative electrodes, sometimes causing short circuit.

[0009] Thereupon, regarding the lithium battery, the research and development of a lithium ion battery incorporating a negative electrode formed by supporting carbon on the collector is now being carried on. This negative electrode does not present the problem with metallic lithium negative electrode during the charging/discharging cycle.

[0010] When a positive electrode of lithium battery is manufactured, predetermined amounts of, for example, LiCoO₂ powder, which is an active material for positive electrode, for example, C powder, which is a conductive material, and, for example, polyvinylidene fluoride, which is a binder, are first mixed to yield a mixed powder, to which a predetermined amount of nonaqueous solvent such as N-methylpyrrolidone is added. The whole mixture is mixed thoroughly, by which a pasted mixture, which is a mixture for positive electrode, is prepared. Then, the mixture is applied onto the surface of collector consisting of metal foil or alloy foil such as Ni, Cu and Ti-Al foil made by, for example, rolling. Thereafter, the mixture for positive electrode is dried to be put on the collector so as to be in firm contact and integral with the collector.

[0011] When a negative electrode of lithium ion battery is manufactured, fiber-form, woven cloth-form, or felt-form carbon fiber itself is sometimes used as C. In general, however, predetermined amounts of C powder, the aforementioned binder powder, and nonaqueous solvent are mixed to prepare a pasted mixture for negative electrode, and the mixture is applied to the collector consisting of a metal foil and pressed on it after being dried.

[0012] An important point for the aforementioned positive and negative electrodes is that the mixture for positive or

negative electrode (hereinafter called the electrode mixture) does not peel off from the collector when the electrode is incorporated into a battery or at the time of charging/discharging cycle. If the mixture peels off from the collector, polarization begins to increase in the process of charging/discharging cycle, which causes the cycle life characteristics to decrease.

5 [0013] When a Ni foam sheet is used as a collector as in the case of the hydrogen-nickel battery, the electrode mixture is less prone to peel off because it fills the inside of the sheet.

[0014] However, the pore diameter of such a foam sheet, which is about 100 µm, is too large with respect to the whole sheet. Therefore, although this pore diameter is preferable from the viewpoint of increased filling amount of electrode mixture and useful to prevent the electrode mixture from peeling off, it decreases the mechanical strength 10 of sheet, so that the sheet is prone to be broken. Also, the filling of electrode mixture is nonuniform, so that the electron transfer reaction in the charging/discharging cycle is prone to be nonuniform.

[0015] When a punching metal sheet, in which openings of a predetermined diameter are formed regularly, for example, in a zigzag lattice pattern, is used as a collector, the opening diameter is too large with respect to the whole sheet as in the case of foam sheet, and in manufacturing, an opening-less sheet must be punched, resulting in an 15 increase in cost.

[0016] Sometimes, an expanded metal is used as a collector. To manufacture the expanded metal, a nonporous sheet must be subjected to special fabrication as in the case of the punching metal sheet, so that the cost of expanded metal is higher than that of punching metal sheet.

20 [0017] In the case of the positive or negative electrode for a lithium battery, as described above, a metal foil usually manufactured by rolling is used as the collector, and paste such as an electrode mixture is simply applied to and pressed on the smooth surface thereof, so that peeling occurs easily.

[0018] For an electrode in which an electrode mixture is supported on both surfaces of the collector, it is very difficult to apply paste to the completely same thickness on both surfaces. The collector used is generally a rolled nonporous foil, so that lithium ions cannot migrate from one surface of the collector to the other surface thereof.

25 [0019] Therefore, during the charging/discharging, it is impossible to completely use the electrode mixture supported on both surfaces of the collector.

[0020] USP 5,441,627 discloses a metal foil manufacturing method in which a metal foil is manufactured by forming a thin metal layer by electrodepositing a metal on the surface of cathode through an electrolytic reaction, and then separating the metal layer from the cathode surface. This document indicates that, in the case when a the surface of 30 a rotating cathode is formed of titanium, it is advisable to adjust the thickness of the anodized film to be formed to 1.4 to 140 angstroms and that when the thickness of the film is greater than 140 angstroms it starts to become an electrical insulator and its insulating properties become nonuniform, the surface of the metal foil obtained being liable to be a surface having unevenness and pinholes so that its mechanical properties are deteriorated.

[0021] An object of the present invention is to provide a method of manufacturing a porous electrolytic metal foil, in 35 which in manufacturing a metal foil by the electrolytic plating method, the metal foil obtained at the same time when the manufacturer proceeds can be made porous.

[0022] Another object of the present invention is to provide a method of manufacturing a porous electrolytic metal foil, in which a porous electrolytic metal foil, which is useful as a collector for a secondary battery electrode, is manufactured continuously and in large quantities, and therefore at a low cost.

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DISCLOSURE OF THE INVENTION

[0023] To achieve the above objects, the present invention provides a method of manufacturing a porous electrolytic metal foil, comprising the steps of:

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continuously forming a metal thin layer by electrically depositing metal ions on the surface of a moving cathode body by an electrolytic reaction which is carried out by immersing an anode body and the moving cathode body in an electrolyte containing metal ions and by applying electric current to between the anode body and moving cathode body while the moving cathode body is moved; and

50 continuously manufacturing an electrolytic metal foil by continuously separating the metal thin layer from the surface of the moving cathode body while the moving cathode body is moved; and further comprising the step of: forming an oxide film.

[0024] FIG. 1 is a schematic sectional view showing a typical cross-sectional structure of a porous electrolytic metal foil manufactured by the method in accordance with the present invention, and FIG. 2 is a schematic sectional view showing a typical cross-sectional structure of an electrode formed by using the metal foil shown in FIG. 1 as a collector and by supporting an electrode mixture on both surfaces thereof.

[0025] In these figures, a metal foil 1 is formed with a plurality of open-pores penetrating in the thickness direction

from one surface 1a thereof to the other surface 1b, and the metal foil has a porous structure as a whole.

[0026] The electrode shown in FIG. 2 has an electrode mixture 3 supported on the surfaces 1a and 1b of the aforesaid metal foil 1. The electrode mixture 3 is supported in such a manner as to get slightly into the open-pore 2 through an opening 2a of the open-pore 2, or in such a manner as to get considerably deep into the open-pore 2 when the open-pore 2 has a large diameter. Alternatively, the electrode mixture 3 is supported in such a manner that the electrode mixtures 3 filled in the open-pore 2 from both surfaces of the metal foil 1 come into contact with each other within the open-pore 2.

[0027] That is, these open-pores 2 offer an anchoring effect to the electrode mixture 3.

[0028] These open-pores 2 are formed randomly, so that not all pores are present as an open-pore penetrating the metal foil 1 from the surface 1a to the surface 1b, and some pores may be closed at an intermediate position.

[0029] For this metal foil 1, it is preferable that the thickness thereof be usually 8 to 100 μm in order to obtain a foil with a porous structure. If the metal foil 1 is too thin, it may be broken in the foil manufacturing process, described later. If it is too thick, the aforesaid open-pores are not formed.

[0030] It is preferable that the diameter of the opening 2a of the open-pore 2 be within the range of 0.1 to 80 μm , though changing depending on the thickness of the metal foil 1. Also, it is preferable that 1 to 500 pores be distributed per unit area (1 mm^2) on the surface of the metal foil 1.

[0031] If the diameter of the open-pore 2 is smaller than 0.1 μm , the electrode mixture 3 does not get into the pore smoothly even if the electrode mixture is applied to and pressed on the metal foil 1, so that the aforementioned anchoring effect is decreased, resulting in a decrease in contact strength between the electrode mixture 3 and the metal foil 1. If the diameter of the open-pore 2 is larger than 80 μm , the mechanical strength of the metal foil 1 decreases, so that the metal foil 1 is broken, for example, when the metal foil 1 is separated from the surface of the moving cathode body in the metal foil manufacturing process, described later.

[0032] If the distribution density of these pores on the surfaces 1a and 1b of the metal foil 1 is lower than 1 pore/ mm^2 , the contact strength between the electrode mixture 3 and the metal foil 1 decreases, so that the electrode mixture is liable to peel off.

[0033] If the distribution density is higher than 500 pores/ mm^2 , though the contact strength between the electrode mixture 3 and the metal foil 1 increases, the metal foil is too porous as a whole, resulting in a decrease in mechanical strength as described above.

[0034] In the electrode manufactured by using the metal foil of the present invention as a collector, the electrode mixture 3 supported on the surfaces 1a and 1b of the metal foil 1 is selected appropriately depending on the battery to be formed.

[0035] For example, when the intended electrode is the positive electrode for a nickel-hydrogen battery, the mixture for positive electrode, in which nickel hydroxide powder is used as an active material, is supported on the surfaces of the metal foil. When it is the negative electrode, the mixture for negative electrode, whose principal ingredient is hydrogen occlusion alloy powder, is supported.

[0036] When the intended electrode is the positive electrode for a lithium battery, the mixture for positive electrode, whose principal ingredient is an active material such as lithium vanadium pentoxide, lithium manganese oxide, and lithium cobalt oxide, is supported on the surfaces of the metal foil. When it is the negative electrode, the mixture for negative electrode, whose principal ingredient is a powder consisting of C such as chips or powder of pyrolytic carbon, coke, graphite, vitreous carbon, resin baked body, activated charcoal, and carbon fiber, is supported.

[0037] The aforementioned metal foil is manufactured continuously as a porous electrolytic metal foil by operating the apparatus described below.

[0038] FIG. 3 is a schematic view showing a typical system used when the porous electrolytic metal foil in accordance with the present invention is manufactured. FIG. 4 is a schematic view showing another system.

[0039] In FIG. 3, an electrolytic bath 4 contains an electrolyte 5 containing metal ions which are the raw material for an electrolytic metal foil to be manufactured, an anode body 6 is disposed in this electrolyte 5, and a drum cathode body 7 facing the anode body 6 is disposed in such a manner that part of the drum cathode body 7 is immersed in the electrolyte 5.

[0040] The anode body 6 is usually made of lead. For the moving cathode body 7, 7', at least the surface thereof is made of stainless steel, Ti, Cr, Al, or Cr-Al alloy.

[0041] Electrolytic reaction is carried out by applying electric current to between the anode body 6 and the drum cathode body 7 while the drum cathode body 7 is rotated in the direction indicated by arrow p to move the surface thereof successively in the electrolyte 5 and while the electrolyte 5 is supplied continuously from a distributor 9 to a gap 8 between the anode body 6 and the drum cathode body 7.

[0042] In the system shown in FIG. 4, a belt cathode body 7' is used in place of the drum cathode body 7 shown in FIG. 3. This belt cathode body 7' is circulated in the direction indicated by arrow p, by which the surface thereof is moved successively in the electrolyte 5.

[0043] In the present invention, the aforementioned drum cathode body 7 and belt cathode body 7' are called a

moving cathode body because the surface thereof on which an electrolytic metal foil is formed moves.

[0044] The metal ions are electrically deposited on the surface of the drum cathode body 7 or belt cathode body 7', where a metal thin layer is continuously formed so that the layer thickness increases successively in the moving direction of the surface of the drum cathode body 7 or belt cathode body 7'. This metal thin layer is separated from the surface of the drum cathode body 7 or belt cathode body 7' at a point where the surface emerges from the electrolyte, and wound around a take-up roll 11 as the electrolytic metal foil 1 via rolls 10a and 10b.

[0045] In the method of the present invention, an exposed surface 7a, 7'a, which is exposed on the drum cathode body 7 or belt cathode body 7' by the separation of the metal thin layer from the surface of the drum cathode body 7 or belt cathode body 7', is subjected to surface treatment, described later.

[0046] This surface treatment is carried out to form a film consisting of an electrical insulating material on the exposed surface 7a, 7'a of the moving cathode body 7, 7'.

[0047] Specifically, the surface treatment includes,

a treatment for forming an oxide film with a thickness of more than 14 nm on the exposed surface 7a, 7'a by applying electrolytic oxidation to the exposed surface 7a, 7'a (called a first surface treatment).

[0048] The following is a detailed description of these surface treatments.

[0049] First, the first surface treatment will be described. As shown in FIGS. 3 and 4, a oxide film forming apparatus A, described later, is mounted on the exposed surface 7a, 7'a of the moving cathode body 7, 7' from which the metal thin layer is separated. By operating this apparatus A, the exposed surface 7a, 7'a is electrolytically oxidized in the process before the exposed surface 7a, 7'a is immersed again in the electrolyte 5, so that an oxide film with a thickness of more than 14 nm is formed on the whole surface.

[0050] If the aforesaid metal thin layer is formed on the surface of the drum cathode body 7 or belt cathode body 7' with the oxide film formed on the surface, the metal thin layer is made to have a porous structure having open-pores. When the electrolytic metal foil is formed by separating the metal thin layer from the moving cathode body such as the drum cathode body 7 or belt cathode body 7', both of the surface (S surface) on the moving cathode body side and the opposite surface (M surface) become rough. Moreover, the opposite surface becomes rougher than the surface on the moving cathode body side.

[0051] At this time, if the formed oxide film is made thinner than 14 nm, the metal thin layer formed on the oxide film is difficult to have a proper porous structure having the aforesaid open-pores and the distribution density thereof. This decreases the performance of metal foil as a collector on which the electrode mixture as described above is supported with a high contact strength.

[0052] However, if the oxide film is made too thick, the metal thin layer formed on the oxide film becomes excessively porous, by which the mechanical strength thereof is decreased, so that a trouble such that the metal thin layer is broken when it is separated from the moving cathode body occurs frequently. Therefore, it is preferable that the thickness of the oxide film be not greater than 100 nm.

[0053] The apparatus A for forming the oxide film, which functions in the above-described manner, on the exposed surface of the moving cathode body includes holding means for holding an electrolytic treatment liquid for electrolytic oxidation so that the treatment liquid is in contact with the exposed surface of the moving cathode body; a counter electrode body disposed in the holding means so as to oppose to the exposed surface of the moving cathode body; and supply means for supplying the electrolytic treatment liquid to the holding means.

[0054] This apparatus A anodizes the exposed surface by applying electric current to between the moving cathode and the counter electrode body with the electrolytic treatment liquid supplied continuously from the supply means to the holding means and with the electrolytic treatment liquid in contact with the exposed surface of the moving cathode body while the metal thin layer is formed on the surface of the moving cathode body by applying electric current to between the anode body and the moving cathode body to continue electrolytic plating, without stopping the operation of the moving cathode body.

[0055] At this time, the operation is performed so that the operation potential is lower in the order of the anode body, moving cathode body, and counter electrode body. This is because if the operation potential does not establish the above relationship, the exposed surface of the moving cathode body is not electrolytically oxidized, so that the oxide film is not formed there.

[0056] The oxide film may be formed continuously or intermittently using the apparatus A.

[0057] When the metal thin layer formed by electric deposition is separated from the surface of the moving cathode body, part of the oxide film is removed to the metal thin layer side at the same time, so that the thickness of the oxide film is decreased gradually by the repetition of electric deposition and separation. Therefore, the metal thin layer formed on the oxide film does not become to have the proper porous structure as described above. To compensate the decreased thickness, the oxide film must be formed continuously or intermittently.

[0058] To operate the apparatus A, the constant current method or constant voltage method can be used. Of these two methods, the constant voltage method is preferable because the part of oxide film removed from the surface of the moving cathode body can be compensated automatically and instantly, and the thickness of the oxide film can be

prevented from increasing up to the unnecessary thickness.

[0059] An example A₁ of the apparatus A will be described with reference to the drawing.

[0060] FIG. 5 is a partially cutaway perspective view showing a state in which an apparatus A₁ is mounted on the exposed surface 7a of the drum cathode body 7.

5 [0061] This apparatus A₁, having a shaft 12 for mounting the apparatus at the center r, comprises a conductive roll 13 functioning as a counter electrode body opposing to the drum cathode body 7 in electrolytic oxidation, electrolytic treatment liquid holding means 14 disposed around the conductive roll 13, and a pipe which is electrolytic treatment liquid supply means 15 for supplying electrolytic treatment liquid 15a used for electrolytic oxidation to the electrolytic treatment liquid holding means 14. By rotatably supporting the shaft 12 by not-illustrated means with the electrolytic treatment liquid holding means 14 in contact with the exposed surface 7a of the drum cathode body 7 indicated by an imaginary line, the whole of the apparatus A₁ is mounted on the exposed surface 7a of the drum cathode body 7 as shown in FIG. 3.

10 [0062] The conductive roll 13 may be a roll the whole of which is made of a corrosion-resistant material such as titanium, nickel, chromium, copper, and stainless steel or a roll in which the surface of the above material is coated with a material having electric conductivity and resistance to corrosion caused by the electrolytic treatment liquid 15a used to form the oxide film, such as silver, silver alloy, gold, gold alloy, palladium, and palladium alloy. Also, the surface of a roll made of a non-conductive plastic material such as polypropylene or polyvinyl chloride may be covered with foil, wire, or mesh of a material having electric conductivity and corrosion resistance. Alternatively, a material having electric conductivity and corrosion resistance may be plated, thermally sprayed, or applied to the surface of the aforementioned roll. To sum up, a roll at least the surface of which has electric conductivity and corrosion resistance is used as a counter electrode body for electrolytic oxidation on the surface of the drum cathode body.

15 [0063] The electrolytic treatment liquid holding means 14 surrounding the conductive roll (counter electrode body) 13 has a proper elasticity as well as permeability. The electrolytic treatment liquid holding means 14 is formed by covering the outer periphery of the conductive roll 13 with a material having resistance to corrosion caused by the electrolytic treatment liquid used, such as felt, nonwoven fabric cloth, or split yarn of polyurethane, polyvinyl formal, or polyester.

20 [0064] Above the electrolytic treatment liquid holding means 14, the pipe 15 formed with a plurality of openings 15b in the axial direction of the electrolytic treatment liquid holding means 14 is disposed as electrolytic treatment liquid supply means, and the predetermined electrolytic treatment liquid 15a is supplied to the pipe 15 by means of a pump 30 15c. The supplied electrolytic treatment liquid 15a is not subject to any special restriction, and a liquid which does not have an adverse effect on the manufacture of metal thin layer even if being mixed with the electrolyte used for the manufacture of metal thin layer is used. For example, a liquid which is the same as the electrolyte used at present to make metal electrically deposit on the surface of the drum cathode body, or a liquid which has the same components as those of the electrolyte but a different ratio of components can be used.

35 [0065] As the electrolyte, for example, copper sulfate solution is used in manufacturing electrolytic copper foil, and nickel sulfate solution or nickel sulfamate solution is used in manufacturing electrolytic nickel foil. Also, in manufacturing electrolytic aluminum foil, AlCl₃-LiAlH₄-tetrahydrofuran bath and NaF · 2Al(C₂H₅O)₃ · 4 toluene bath, which are disclosed in Japanese Patent Publication No. 48-4460, and the like can be used.

40 [0066] As the electrolytic treatment liquid 15a, a liquid which does not contain ions of metal deposited on the drum cathode body 7 can also be used. Such electrolytic treatment solutions include an acidic solution such as sulfuric acid solution, phosphoric acid solution, and hydrochloric acid solution and a neutral solution in which sodium sulfate, potassium sulfate, sodium hydrochloride, potassium hydrochloride, etc. are dissolved. Among these, sulfuric acid solution is preferably used in manufacturing electrolytic copper foil by using copper sulfate electrolyte.

45 [0067] The supply means for the electrolytic treatment liquid 15a is not limited to the above-mentioned pipe-form means. For example, the conductive roll 13 is made hollow, many openings are formed on the peripheral surface thereof, and the electrolytic treatment liquid 15a is supplied to the hollow portion of the conductive roll 13, by which the electrolytic treatment liquid 15a may be supplied to the electrolytic treatment liquid holding means 14 from the inside thereof through the openings on the peripheral surface of the conductive roll 13.

50 [0068] When the apparatus A₁ is used, the oxide film is formed on the exposed surface 7a of the drum cathode body 7 in the following manner.

55 [0069] First, the electrolytic treatment liquid holding means 14 of the apparatus A₁ is elastically brought into contact with the exposed surface 7a of the drum cathode body 7 rotating in the direction indicated by arrow p. Thereupon, the electrolytic treatment liquid holding means 14 rotates automatically in the direction indicated by arrow r in FIG. 5. With this state being kept, a predetermined electrolytic treatment liquid 15a is supplied to the pipe (electrolytic treatment liquid supply means) 15.

[0070] The electrolytic treatment liquid 15a drips onto the electrolytic treatment liquid holding means 14 from the openings 15b, permeates into the electrolytic treatment liquid holding means 14, and is kept therein. As a result, the conductive roll (counter electrode body for electrolytic oxidation) 13 and the exposed surface 7a of the drum cathode

body 7 becomes conductive via the electrolytic treatment liquid 15a.

[0071] Then, terminals 13a, 13a attached to the conductive roll 13 are connected to the minus side of a power supply (not shown), and the exposed surface 7a of the drum cathode body 7 is connected to the plus side of the power supply so that an electrolytic current flows between the conductive roll 13 and the exposed surface 7a of the drum cathode body 7, whereby the exposed surface 7a is anodized. At this time, the conductive roll (counter electrode body) 13 is operated so that the potential becomes to be lower than the potential of the drum cathode body in the electrolytic bath on which surface is formed a metal thin layer, and at the same time, the potential of the anode body positioned in the electrolytic bath is made higher than that of the drum cathode body. If the potential of the drum cathode body is higher than that of the anode body, there occurs a trouble such that metal is not electrically deposited on the surface of the drum cathode body, or a trouble such that if electric current is applied so that the potential of the conductive roll is higher than that of the drum cathode body, the conductive roll 13 is made the plus electrode, and the exposed surface 7a of the drum cathode body 7 is made the minus electrode, so that the exposed surface 7a of the drum cathode body 7 is not electrolytically oxidized.

[0072] By properly selecting the rotational speed of the drum cathode body 7, the operation potential of the conductive roll (counter electrode body), and the like, an oxide film with a desirable thickness is formed on the exposed surface 7a.

[0073] In this apparatus A₁, it is preferable that the width of the electrolytic treatment liquid holding means 14 is smaller than that of the drum cathode body 7 so that both side portions 7b, 7b on the exposed surface 7a of the drum cathode body 7 are not electrolytically oxidized.

[0074] The reason for this is as follows: The metal thin layer directly formed at these portions 7b, 7b has a higher mechanical strength than the porous metal thin layer formed on the oxide film produced by the apparatus A₁. Therefore, when the metal thin layer is separated from the drum cathode body, a trouble of breaking of the metal thin layer in the process of separation can be prevented by starting the separation from the portion of metal thin layer formed at the portions 7b, 7b.

[0075] FIG. 6 is a partially cutaway perspective view showing a state in which another apparatus A₂ is mounted on the exposed surface 7a of the drum cathode body 7.

[0076] In the case of this apparatus A₂, the electrolytic treatment liquid holding means 16 is a box-shaped vessel whose one face is open, and this opening 16a is disposed in liquid-tight slidable contact with or close to the exposed surface 7a of the drum cathode body 7. Therefore, the portions of sides 16b, 16b of the vessel 16, which are in slidable contact with or close to the exposed surface 7a of the drum cathode body 7, are curved so as to match the curvature of the exposed surface 7a of the drum cathode body 7.

[0077] The width of the vessel 16 is smaller than that of the drum cathode body 7 for the same reason as that in the case of the electrolytic treatment liquid holding means 14 for the apparatus A₁, so that both side portions 7b, 7b of the exposed surface 7a of the drum cathode body 7 are not electrolytically oxidized.

[0078] It is preferable that the vessel 16 be made of a material which is resistant to corrosion caused by the electrolytic treatment liquid used, such as polyvinyl chloride and polypropylene.

[0079] In the case where the vessel 16 is disposed so as to be in slidable contact with the exposed surface 7a of the drum cathode body 7, it is preferable that the vessel 16 be made of a material having wear-resistance, lubricity, and elasticity, such as polyethylene, polyester, polyurethane, and silicone rubber. In this vessel 16, a counter electrode body 17 for electrolytic oxidation, which is made of, for example, titanium or stainless steel, is disposed. This counter electrode body 17 faces the exposed surface 7a of the drum cathode body 7 exposed to the interior of the vessel 16 through the opening 16a of the vessel 16.

[0080] A supply pipe 18a for electrolytic treatment liquid is attached to the side wall of the vessel 16, and a discharge pipe 18b for electrolytic treatment liquid is attached to the top wall thereof, these pipes constituting electrolytic treatment liquid supply means 18. The electrolytic treatment liquid used to form an oxide film is supplied into the vessel 16 through the supply pipe 18a to fill the vessel 16, covers the exposed surface 7a of the drum cathode body 7, and flows out of the system through the discharge pipe 18b.

[0081] Electric current is applied to between the counter electrode body 17 and the drum cathode body 7 while allowing the electrolytic treatment liquid to flow in the vessel 16, by which the exposed surface 7a of the drum cathode body which is exposed to the interior of the vessel 16 through the opening 16a can be electrolytically oxidized.

[0082] If the vessel 16 is mounted so that some clearance is formed between the opening 16a of the vessel 16 and the exposed surface 7a of the drum cathode body 7, part of the supplied electrolytic treatment liquid flows out along the exposed surface 7a of the drum cathode body 7 through the clearance, so that an electrolytic treatment liquid film with a uniform thickness is formed on the exposed surface 7a of the drum cathode body which is exposed to the interior of the vessel 16 through the opening 16a, by which the forming condition of oxide film is preferably stabilized.

[0083] For the electrolytic treatment liquid supplied into the vessel 16, the electrolyte used for manufacturing a metal thin layer is usually used as it is by being pumped up.

[0084] FIG. 7 and FIG. 8, which is a sectional view taken along the line VIII-VIII of FIG. 7, are views showing a state in which another apparatus A₃ is mounted on the exposed surface of the drum cathode body.

- [0085] This apparatus A₃ has electrolytic treatment liquid holding means consisting of a trough-shaped vessel 19. For this trough-shaped vessel 19, the upper part is open, and both of the ends 19a, 19a in the lengthwise direction are sealed. One end 19a is provided with a supply pipe 20 for electrolytic treatment liquid, constituting electrolytic treatment liquid supply means. One side 19b of the trough-shaped vessel 19 is lower in height than the other side 19c.
- 5 [0086] The length of the trough-shaped vessel 19 is shorter than the width of the drum cathode body 7 for the same reason as that in the case of the electrolytic treatment holding means 15 of the apparatus A₁, so that both side portions 7b, 7b of the exposed surface 7a of the drum cathode body 7 are not electrolytically oxidized.
- 10 [0087] The trough-shaped vessel 19 is mounted so that the lengthwise direction thereof agrees with the width direction of the drum cathode body 7, and the one side 19b is close to the exposed surface 7a of the drum cathode body so as to form some clearance between the side 19b and the exposed surface 7a of the drum cathode body.
- 15 [0088] A counter electrode body 17 is disposed on the other side 19c of the trough-shaped vessel 19, and a metal powder removing filter 21 is interposed between the counter electrode body 17 and the exposed surface 7a of the drum cathode body. As a result, the interior of the trough-shaped vessel 19 is divided into a space 19d where the counter electrode body 17 is disposed and a space 19e positioned on the side of the exposed surface 7a of the drum cathode body.
- 20 [0089] The metal powder removing filter 21 prevents metal powder from depositing on the exposed surface 7a of the drum cathode body 7, the metal powder being deposited on the exposed surface 7a of the drum cathode body 7 by a process in which the metal contained in the electrolytic treatment liquid is electrically deposited abnormally as metal powder on the surface of the counter electrode body 17 in the electrolytic treatment, and the metal powder is removed from the counter electrode body by the flow of electrolytic treatment liquid.
- 25 [0090] The electrolytic treatment liquid supplied to the trough-shaped vessel 19 through the supply pipe 20 overflows over the side 19b after filling the trough-shaped vessel 19, and flows down along the exposed surface 7a of the drum cathode body rotating in the direction indicated by arrow p. In this process, therefore, an electrolytic treatment liquid film with a uniform thickness is continuously formed on the exposed surface 7a of the drum cathode body.
- 30 [0091] For the electrolytic treatment liquid, the electrolyte used for manufacturing a metal thin layer may be used as it is. Alternatively, electrolytic treatment liquid supply pipes connecting with the spaces 19d and 19e formed in the trough-shaped vessel 19 may be disposed separately so that, for example, the electrolyte used for manufacturing a metal thin layer is supplied to the space 19d and an electrolyte with a different composition or containing no metal ions is supplied to the space 19e.
- 35 [0092] The cross-sectional shape of the trough-shaped vessel 19 is not limited to a triangular one as shown in FIGS. 7 and 8. The shape may be a polygon such as quadrangle and hexagon or a semicircle. In effect, the trough-shaped vessel 19 may be shaped so that the electrolytic treatment liquid filling the vessel 19 overflows over the side 19b so that a liquid film can be formed on the exposed surface 7a of the drum cathode body.
- 40 [0093] FIG. 9 and FIG. 10, which is a sectional view taken along the line X-X of FIG. 9, are views showing a state in which still another apparatus A₄ is mounted on the exposed surface of the drum cathode body.
- 45 [0094] This apparatus A₄ has electrolytic treatment liquid holding means 22 consisting of an elongated closed vessel of a convex lens shape in cross section.
- [0095] Specifically, an attaching portion 22b of a counter electrode body 17 for electrolytic oxidation is mounted at the back of a curved plate 22a in a liquid tight manner, both ends 22C, 22C in the lengthwise direction are sealed, a supply pipe 23 for electrolytic treatment liquid is attached to a substantially central position of vessel, and electrolytic treatment liquid spraying means 22d is formed at the tip end of the curved plate 22a, by which the electrolytic treatment liquid supply means for supplying electrolytic treatment liquid onto the exposed surface 7a of the drum cathode body 7 is formed. The spraying means 22d may consist of, for example, a plurality of holes formed along the lengthwise direction of the curved plate 22a or a slit with a predetermined width formed in the lengthwise direction of the curved plate 22a.
- 50 [0096] The length of the closed vessel 22 is shorter than the width of the drum cathode body 7 for the same reason as that in the case of the electrolytic treatment holding means 15 of the apparatus A₁, so that both side portions 7b, 7b of the exposed surface 7a of the drum cathode body 7 are not electrolytically oxidized.
- 55 [0097] The whole vessel is so configured that the counter electrode body 17 is disposed at the attaching portion 22b, the lengthwise direction of the vessel agrees with the width direction of the drum cathode body 7, and spraying means 22d formed in the curved plate 22a is disposed so as to face the exposed surface 7a of the drum cathode body 7 with a predetermined gap.
- [0098] The electrolytic treatment liquid fed into the vessel 22 through the supply pipe 23 by pumping etc. is sprayed from the spraying means 22d after filling the vessel 22 to hit the exposed surface 7a of the drum cathode body 7 rotating in the direction indicated by arrow p, and flows down along the exposed surface 7a, whereby a liquid film with a uniform thickness is formed.
- [0099] As the electrolytic treatment liquid, the electrolyte used for manufacturing a metal thin layer may be used, and if necessary, another electrolyte such as dilute sulfuric acid solution may be used.

[0100] While this state is maintained, a predetermined voltage is applied to between an anode of the drum cathode body 7 and a cathode of the counter electrode body 17, by which the exposed surface 7a of the drum cathode body is electrolytically oxidized. Since the drum cathode body 7 is rotated in the direction indicated by arrow p in the figures, an oxide film is formed continuously or intermittently on the exposed surface 7a.

5 [0101] Although in this apparatus A₄, the surface opposing to the exposed surface 7a of the drum cathode body is curved, the shape is not limited to this one, and any shape such that the electrolytic treatment liquid filling the vessel interior can be sprayed toward the exposed surface 7a of the drum cathode body may be used. Also, means for uniformly distributing the electrolytic treatment liquid, for example, means in which uniform small holes are formed in a pipe and the electrolytic treatment liquid supplied to this pipe is sprayed from these small holes may be provided within the
10 vessel 22. Further, the supply pipe 23 is not necessarily attached to the central position of the apparatus A₄, but may be attached to any position where the electrolytic treatment liquid can be sprayed uniformly from the spraying means 22d.

15 [0102] Also, a metal powder removing filter may be provided between the counter electrode body 17 and the spraying means 22d as in the case of the apparatus A₃ so as to prevent the metal powder electrically deposited on the counter electrode body from flowing out onto the exposed surface 7a of the drum cathode body 7.

20 [0103] This apparatus A₄ achieves an effect that when the electrolyte for manufacturing a metal thin layer, which has a relatively high metal concentration, is used as the electrolytic treatment liquid, the amount of electrolyte used can be decreased by making the spray opening of the spraying means 22d smallest possible, and the deposition of metal salt in the electrolytic treatment liquid used can be inhibited to the utmost by decreasing the amount of scattered electrolyte.

25 [0104] For example, when an electrolytic copper foil is manufactured by using copper sulfate electrolyte, copper sulfate solution having a relatively high copper concentration is used as an electrolyte. When this electrolyte is used as an electrolytic treatment liquid for forming an oxide film, copper sulfate crystals are produced if the temperature is low, and stick to the apparatus and the electrolytic copper foil, thereby inhibiting the smooth operation of the apparatus.
In the apparatus A₄ shown in FIGS. 9 and 10, this trouble can be eliminated easily by merely changing the shape of the spraying means 22d and the distance from the spraying means 22d to the exposed surface 7a of the drum cathode body.

BRIEF DESCRIPTION OF THE DRAWINGS

30 [0105]

FIG. 1 is a sectional view showing a typical cross-sectional structure of a metal foil manufactured by a method in accordance with the present invention;
35 FIG. 2 is a sectional view of a typical electrode with a collector using a metal foil manufactured by a method in accordance with the present invention;
FIG. 3 is a schematic view showing a manufacturing system for an electrolytic metal foil;
FIG. 4 is a schematic view showing another manufacturing system;
40 FIG. 5 is a partially cutaway perspective view showing a state in which an apparatus A₁ used for forming an oxide film is mounted on the exposed surface of a drum cathode body;
FIG. 6 is a partially cutaway perspective view showing a state in which an apparatus A₂ used for forming an oxide film is mounted on the exposed surface of a drum cathode body;
45 FIG. 7 is a partially cutaway perspective view showing a state in which an apparatus A₃ used for forming an oxide film is mounted on the exposed surface of a drum cathode body;
FIG. 8 is a sectional view taken along the line VIII-VIII of FIG. 7;
FIG. 9 is a partially cutaway perspective view showing a state in which an apparatus A₄ used for forming an oxide film is mounted on the exposed surface of a drum cathode body; and
FIG. 10 is a sectional view taken along the line X-X of FIG. 9.

50 **BEST MODE OF CARRYING OUT THE INVENTION**

Working examples 1 and 2, comparative examples 1 and 2

1) Manufacture of metal foil

55 [0106] In the system shown in FIG. 3, the drum cathode body 7 was made of titanium, and the apparatus A₄ shown in FIGS. 9 and 10 was mounted on the surface of the drum cathode body 7.

[0107] The electrolyte 5 with a copper ion concentration of 100 g/liter, a sulfuric acid concentration of 100 g/liter, and

- a bath temperature of 60°C was supplied into the electrolytic bath 4. While the drum cathode body 7 was rotated, an electric current with a current density of 60 A/dm² was applied to between the drum cathode body 7 and the anode body 6 to continuously form a copper thin layer on the surface of the drum cathode body 7. By separating the copper thin layer from the surface of the drum cathode body 7, the electrolytic copper foil 1 was manufactured continuously.
- 5 [0108] While the manufacture of the electrolytic copper foil 1 was continued, the aforesaid electrolyte was supplied into the closed vessel 22 through the supply pipe 23 of the apparatus A₄, and sprayed onto the exposed surface 7a of the drum cathode body 7 rotating in the direction indicated by arrow p from the spraying means 22d while the voltage between the drum cathode body 7 and the counter electrode body (made of titanium) 17 was kept at a constant value of 50 V.
- 10 [0109] A titanium oxide film with a thickness of 70 nm was formed continuously on the exposed surface 7a of the drum cathode body 7.
- [0110] Copper was electrically deposited on this titanium oxide film to form a copper thin layer. By continuously separating the copper thin layer from the drum cathode body 7, the electrolytic copper foil 1 was obtained.
- 15 [0111] Then, the obtained electrolytic copper foil 1 was subjected to surface roughening with a current density of 30 A/dm² by using an electrolyte with a copper ion concentration 5 of 20 g/liter, a sulfuric acid concentration of 40 g/liter, and a bath temperature of 30°C.
- [0112] For the electrolytic copper foil after surface roughening, the average thickness was 50 µm, and the surface roughnesses (Rz) of the separation surface (S surface) from the drum cathode body and the opposite surface (M surface) were 5 µm and 11 µm, respectively.
- 20 [0113] Also, in this electrolytic copper foil, open-pores communicating in the thickness direction were found. The diameter of the open-pore was 0.1 to 3 µm, and the distribution density thereof was 100 to 200 pores/mm².

2) Manufacture of electrode

- 25 [0114] Ten parts by weight of polyvinylidene fluoride powder was mixed with 100 parts by weight of KETJEN BLACK EC(carbon black manufactured by AKZO CO., LTD., specific surface area: 950 m²/g, average grain size: 0.03 µm), and 30 parts by weight of N-methylpyrrolidone was added to the resultant mixed powder to prepare paste of active material mixture.
- 30 [0115] This paste was applied to both of the surfaces of the aforesaid electrolytic copper foil, dried, and press-formed at a pressure of 2000 kg/cm² to manufacture a working example electrode 1 of 100 µm thick, 10 mm wide, and 20 mm long. The amount of active material mixture supported on this electrode was 20 mg.
- [0116] For comparison, a rolled copper foil of 50 µm thick was prepared, and 20 mg of an active material mixture was put on both of the surfaces thereof in the same way as described above to manufacture a comparative example electrode 1.
- 35 [0117] Also, both of the surfaces of the aforesaid rolled copper foil were roughened to about Rz 2 to 5 µm with #800 emery paper, and 20 mg of an active material mixture was put thereon in the same way as in the working examples to manufacture a comparative example electrode 2.

3) Cycle life of electrode

- 40 [0118] An electrolyte formed by dissolving lithium perchlorate of 1 M in propylene carbonate of 1 kg was prepared. Each of the aforesaid electrodes was disposed in this electrolyte as a negative electrode, and metallic lithium foils were disposed as a counter electrode and a reference electrode, by which four kinds of three-electrode cells were assembled.
- 45 [0119] Then a charging/discharging cycle test was made. In one cycle of this test, a constant current of 1.2 mA was applied to the aforesaid three-electrode cell to perform charging until the voltage reached 0 V with respect to the potential of the reference electrode, the current application was halted for 20 minutes, and then discharging was performed with a constant current of 1.2 mA until the voltage reached 1.5 V with respect to the potential of the reference electrode.
- [0120] For each three-electrode cell, the discharge capacity at the 20th cycle in the charging/discharging cycle test was compared with the discharge capacity at the 1st cycle, and the ratio (%) of the former to the latter was calculated. The result is given in Table 1.

Table 1

	Ratio of discharge capacity in charging/discharging cycle test (%: 20th cycle/ 1st cycle)
Working example electrode 1	97 or higher

Table 1 (continued)

	Ratio of discharge capacity in charging/discharging cycle test (%: 20th cycle/ 1st cycle)
5	
Comparative example electrode 1	About 40
Comparative example electrode 2	About 70

- 10 [0121] As is apparent from the above result, the discharge capacity of the working example electrode is less prone to decrease in the process of charging/discharging cycle, so that the working example electrodes have excellent cycle life characteristics.
- [0122] The reason for this is that because the collector (electrolytic copper foil) has a porous structure of the aforesaid specification, the contact strength between the collector and the active material mixture supported on the collector is high, so that the active material mixture is effectively prevented from peeling off in the process of the charging/discharging cycle test. Also, the reason for this is thought to be that because the electrolytic copper foil is porous and open-pores penetrate the foil in the thickness direction, lithium ions pass through the open-pores between the active material mixtures supported on the surfaces, so that a uniform electron transfer reaction proceeds.

20 Working example 2

- [0123] The apparatus A₃ shown in FIGS. 7 and 8 was mounted on the exposed surface of a titanium-made drum cathode body. An electrolytic copper foil was manufactured while a 35 nm thick titanium oxide film was formed on the exposed surface 7a of the drum cathode body 7 by applying a constant voltage of 25 V to between the counter electrode body 17 and the drum cathode body 7. The resultant electrolytic copper foil was subjected to surface roughening under the same conditions as in the case of the working example electrode 1.
- [0124] The obtained electrolytic copper foil had a porous structure in which the average thickness was 25 µm, the Rz of S surface was 2 µm, the Rz of M surface was 9 µm, the diameter of open-pore was 0.1 to 3 µm, and the distribution density thereof was 150 to 250 pores/mm².
- [0125] A collector with an average thickness of 50 µm whose surface consisted of the M surface was formed by lapping the electrolytic copper foil over another with their S surfaces being brought into contact with each other, and an active material mixture was put on the M surfaces in the same way as in the case of the working example electrode 1, by which a working example electrode 2 was manufactured.
- [0126] This electrode was subjected to the same charging/discharging cycle test as in the case of the working example electrode 1.
- [0127] This electrode showed a value of 98% or higher of the ratio of discharge capacity at the 20th cycle to discharge capacity at the 1st cycle, exhibiting excellent cycle life characteristics.

40 Working example 3

- [0128] The apparatus A₁ shown in FIG. 5 was mounted on the exposed surface of a titanium-made drum cathode body. An electrolytic copper foil was manufactured while a 70 nm thick titanium oxide film was formed on the exposed surface 7a of the drum cathode body 7 by applying a constant voltage of 50 V to between the conductive roll 13 and the drum cathode body 7.
- [0129] The obtained electrolytic copper foil had a porous structure in which the average thickness was 20 µm, the Rz of S surface was 2 µm, the Rz of M surface was 6 µm, the diameter of open-pore was 0.1 to 3 µm, and the distribution density thereof was 350 to 450 pores/mm².
- [0130] After an active material mixture was put on the M surface and S surface of this electrolytic copper foil in such a manner that the ratio of amount of mixture supported on the M surface to that on the S surface is 9:1, the electrolytic copper foil was lapped over another with their S surface sides being brought into contact with each other in the same way as in the case of the working example electrode 2, and the lapped foils were dried and press-formed at a pressure of 2000 kg/cm², by which a working example electrode 3 was manufactured.
- [0131] This electrode was subjected to the same charging/discharging cycle test as in the case of the working example electrode 1.
- [0132] This electrode showed a value of 99% or higher of the ratio of discharge capacity at the 20th cycle to discharge capacity at the 1st cycle, exhibiting excellent cycle life characteristics.

Working example 4

[0133] Commercially available lithium carbonate (Li_2CO_3) and basic cobalt carbonate ($2\text{CoCO}_3 \cdot 3\text{Co(OH)}_2$) were weighed so that the molar ratio of Li/Co is 1:1, and wet-blended using ethanol with a zirconia-made ball mill. Thereafter, the blended material was heat-treated at a temperature of 900°C for two hours to synthesize LiCoO_2 .

[0134] This LiCoO_2 was ground into powder with an average grain size of 16 μm with the ball mill, and 6 parts by weight of graphite powder with an average grain size of 0.1 μm was blended with 100 parts by weight of this powder. Further, 3.5 parts by weight of polyvinylidene powder was dissolved in 30 parts by weight of N-methylpyrrolidone, and the resultant material was added to the aforesaid mixed powder of LiCoO_2 powder and graphite powder to prepare paste of active material mixture (electrode mixture).

[0135] Using this paste and using the electrolytic copper foil shown in the working example electrode 1 as a collector, a working example electrode 4 with the active material mixture of 20 mg was manufactured in the same way as in the case of the working example electrode 1.

[0136] This electrode was subjected to the same charging/discharging cycle test as in the case of the working example electrode 1.

[0137] This electrode showed a value of 98% or higher of the ratio of discharge capacity at the 20th cycle to discharge capacity at the 1st cycle, exhibiting excellent cycle life characteristics.

Working example 5

[0138] In working example 1, the electrolyte was replaced with an electrolyte for manufacturing electrolytic nickel foil, having a nickel sulfate concentration of 300 g/liter, a boric acid concentration of 40 g/liter, and a bath temperature of 60°C, and this electrolyte was used to form a 70 nm thick titanium oxide film on the exposed surface of drum cathode body by using the apparatus A₄. While forming this titanium oxide film, an electrolytic nickel foil was manufactured with a current density of 30 A/dm².

[0139] The obtained electrolytic nickel foil had a porous structure in which the average thickness was 25 μm , the Rz of S surface was 2 μm , the Rz of M surface was 7 μm , the diameter of open-pore was 0.1 to 4 μm , the distribution density thereof was 300 to 400 pores/mm², and the porosity was 5%.

[0140] Hydrogen occlusion alloy powder with a composition of $\text{MnNi}_{3.55}\text{Mn}_{0.4}\text{Al}_{0.3}\text{Co}_{0.75}$ (Mn: misch metal) and a grain size of 30 to 50 μm was prepared. Five parts by weight of 60% fluid dispersion of polytetrafluoroethylene powder and 30 parts by weight of 1.2% carboxymethylcellulose solution were mixed with 100 parts by weight of this alloy powder to prepare paste.

[0141] This paste was applied to both of the surfaces of the aforesaid two nickel foils, and one nickel foil was lapped over the other with their S surface sides being brought into contact with each other. After being dried, the lapped foils were press-formed at a pressure of 2000 kg/cm², by which a negative electrode for nickel-hydrogen battery with a thickness of 0.8 mm, a width of 70 mm, and a length of 100 mm was manufactured.

[0142] Meanwhile, a publicly known positive electrode with a thickness of 0.8 mm, a width of 70 mm, and a length of 100 mm was prepared. In this positive electrode, nickel hydroxide was used as an active material for positive electrode, and the theoretical discharge capacity was set at a value about 0.7 times of the theoretical discharge capacity of aforesaid negative electrode. Separators of 0.2 mm thick made of nylon were interposed between four positive electrodes and five negative electrodes, and a 6N KOH electrolyte was used to assemble a nickel-hydrogen battery with a rated capacity of 10 Ah.

[0143] This battery was subjected to a charging/discharging cycle test, in which one cycle consists of 120% overcharging at 0.5 C and discharging down to a final discharge voltage of 1.0 V at 1.0 C, and the decrease ratio of discharge capacity at 500 cycle time was measured.

[0144] For comparison, negative electrodes were manufactured as a comparative example electrode 3 and comparative example electrode 4 by using a punching nickel sheet foil with an opening ratio of 10% and a nickel foam with a porosity of 50% as collectors, respectively, and by putting a mixture on the collector under the same conditions as described above, and nickel-hydrogen batteries were assembled. On these batteries as well, the decrease ratio of discharge capacity at 500 cycle time was measured in the same way as in the working example. The results are given in Table 2.

[0145] In addition, the tensile strength and elongation of the collector were measured by the method specified in JIS C6511, and the measured value is given in Table 2. Also, the manufacturing cost of the comparative example electrode, which is calculated when the manufacturing cost of the working example electrode 5 is taken as 1, is given as a relative value in Table 2.

Table 2

	Decrease ratio of discharge capacity (%: after 500 cycles)	Mechanical properties of collector		Manufacturing cost (relative value)	
		Tensile strength (kg/mm ²)	Elongation (%)		
5	Working example electrode 5	15	25	7	1
10	Comparative example electrode 3	20	15	5	3
15	Comparative example electrode 4	24	5	1	10

[0146] As is apparent from the above result, a battery incorporating an electrode in which a metal foil of the present invention is used as a collector has a low decrease ratio of discharge capacity, and thereby has high cycle life characteristics. Also, the collector has high mechanical properties, so that, for example, breakage or like trouble is not caused even when the collector is contained in the battery by being wound. Because the collector is manufactured by electrolytic plating, it can be mass-produced, so that the manufacturing cost can be reduced, which contributes to the provision of inexpensive electrodes.

INDUSTRIAL APPLICABILITY

[0147] The metal foil manufactured by the method in accordance with the present invention has many open-pores formed in the thickness direction.

[0148] Therefore, when this metal foil is used as a collector for a secondary battery, the openings of these open-pores have an anchoring effect on the electrode mixture supported on the metal foil, so that the contact strength between the electrode mixture and the collector is increased, by which the electrode mixture is prevented from peeling off in the charging/discharging cycle.

[0149] Also, when this metal foil is used as a collector for the electrode of lithium battery, the electron transfer reaction in battery operation proceeds smoothly via the open-pores of this metal foil, so that the coefficient of use of active material is increased, by which, the cycle life characteristics of battery is improved.

[0150] Since this metal foil is manufactured by electrolytic plating, it can be mass-produced, so that the manufacturing cost is decreased, which contributes greatly to the manufacture of inexpensive electrodes.

Claims

1. A method of manufacturing a porous electrolytic metal foil, said foil being formed with a plurality of open-pores penetrating in the thickness direction from one surface thereof to the other surface thereof, comprising the steps of:
 - 45 continuously forming a metal thin layer by electrically depositing metal ions on the surface of a moving cathode body by an electrolytic reaction which is carried out by immersing an anode body and the moving cathode body in an electrolyte containing metal ions and by applying electrical current between the anode body and moving cathode body while said moving cathode body is moved; and
 - 50 continuously manufacturing an electrolytic metal foil by continuously separating said metal thin layer from the surface of said moving cathode body while said moving cathode body is moved;

and further comprising the step of:

55 forming an oxide film on the surface of said moving cathode body exposed after said thin layer is separated, by electrolytic oxidation of said exposed surface;

characterized in that said oxide film is formed with a thickness higher than 14nm and not greater than 100 nm.

Patentansprüch

1. Ein Verfahren zur Herstellung einer porösen elektrolytischen Metallfolie, wobei die Folie mit einer Vielzahl von offenen Poren ausgebildet ist, die in die Dickenrichtung von einer Oberfläche davon zur anderen Oberfläche davon dringen, das folgende Schritte umfasst:
- das kontinuierliche Bilden einer dünnen Metallschicht durch elektrische Ablagerung von Metallionen auf der Oberfläche eines sich bewegenden Kathodenkörpers durch eine elektrolytische Reaktion, die durchgeführt wird, indem ein Anodenkörper und der sich bewegende Kathodenkörper in einen Elektrolyt eingetaucht werden, der Metallionen enthält, und durch das Anlegen von elektrischem Strom zwischen dem Anodenkörper und dem sich bewegenden Kathodenkörper, während der sich bewegende Kathodenkörper bewegt wird; und das kontinuierliche Herstellen einer elektrolytischen Metallfolie durch das kontinuierliche Trennen der dünnen Metallschicht von der Oberfläche des sich bewegenden Kathodenkörpers während der sich bewegende Kathodenkörper bewegt wird;
- und weiterhin den folgenden Schritt umfassend:
- das Bilden eines Oxidfilms auf der Oberfläche des sich bewegenden Kathodenkörpers, die nach der Trennung der dünnen Schicht ausgesetzt ist, durch elektrolytische Oxidierung der ausgesetzten Oberfläche;
- dadurch gekennzeichnet, dass der Oxidfilm mit einer Dicke ausgebildet wird, die höher als 14 nm und nicht größer als 100 nm ist.

Revendications

1. Procédé pour fabriquer une feuille métallique électrolytique poreuse, ladite feuille présentant une pluralité de pores ouverts pénétrant dans la direction de l'épaisseur à partir d'une surface de celle-ci vers l'autre surface de celle-ci, comprenant les étapes de :
- former de façon continue une couche mince métallique en déposant électriquement des ions métalliques sur la surface d'un corps de cathode mobile par une réaction électrolytique qui est mise en oeuvre en immergeant un corps d'anode et le corps de cathode mobile dans un électrolyte contenant des ions métalliques et en appliquant un courant électrique entre le corps d'anode et le corps de cathode mobile, tandis que ledit corps de cathode mobile est déplacé ; et
- fabriquer de façon continue une feuille métallique électrolytique en séparant de façon continue ladite couche mince métallique de la surface dudit corps de cathode mobile, tandis que ledit corps de cathode mobile est déplacé ; et
- comportant de plus l'étape de :
- former un film d'oxyde sur la surface dudit corps de cathode mobile exposée après que ladite couche mince est séparée, par oxydation électrolytique de ladite surface exposée ;
- caractérisé en ce que ledit film d'oxyde est formé en ayant une épaisseur supérieure à 14 nm et pas plus grande que 100 nm.

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FIG. 1

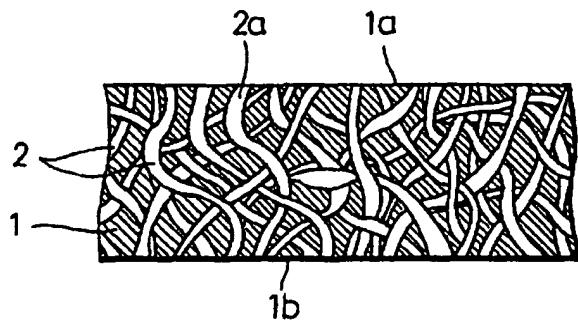


FIG. 2

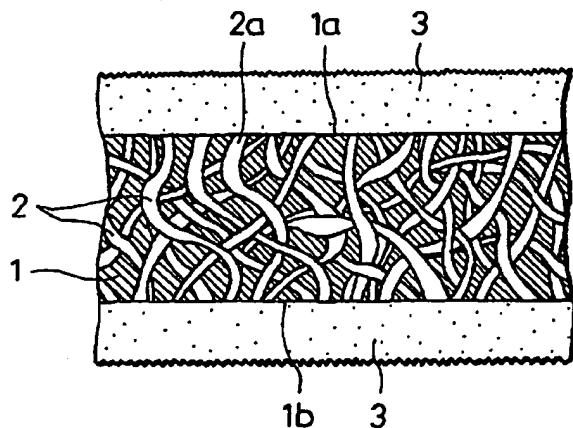


FIG. 3

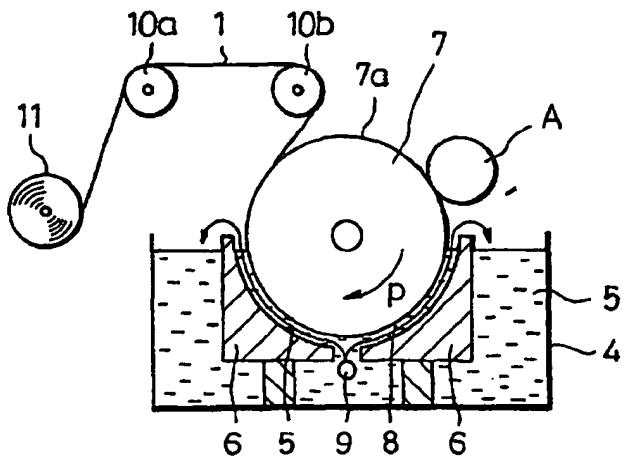


FIG. 4

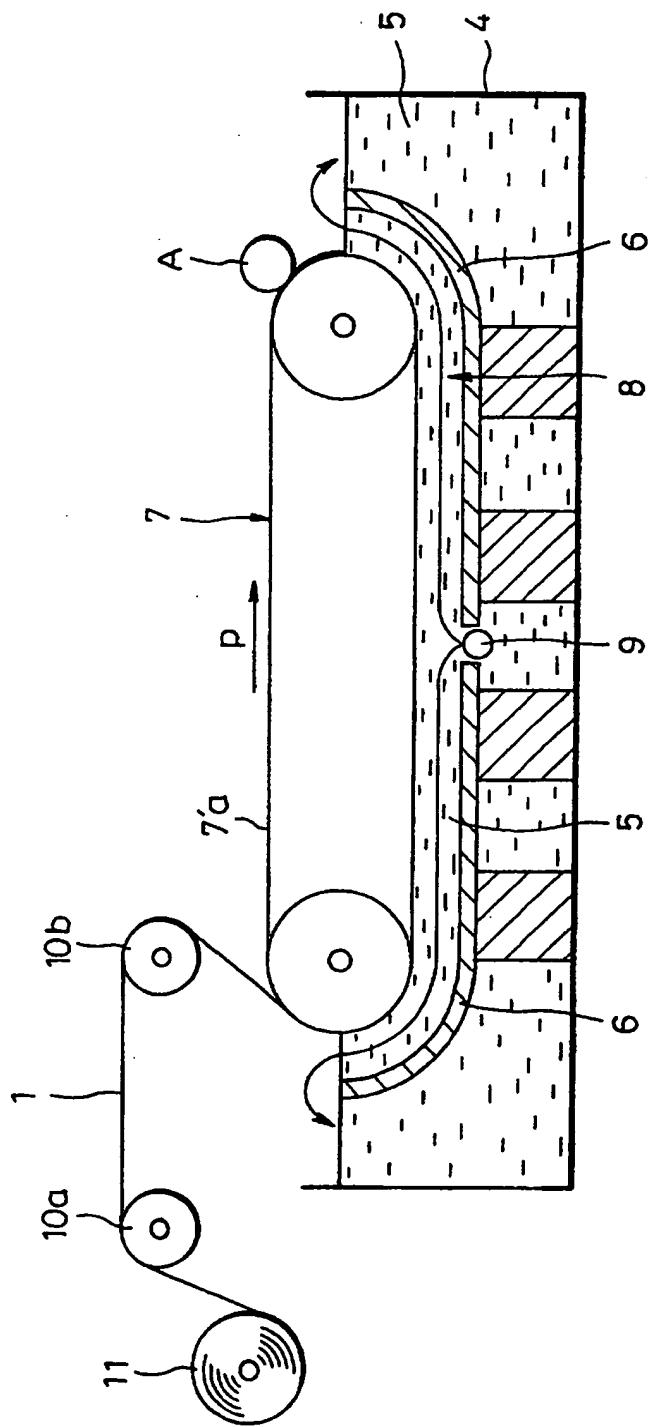


FIG. 5

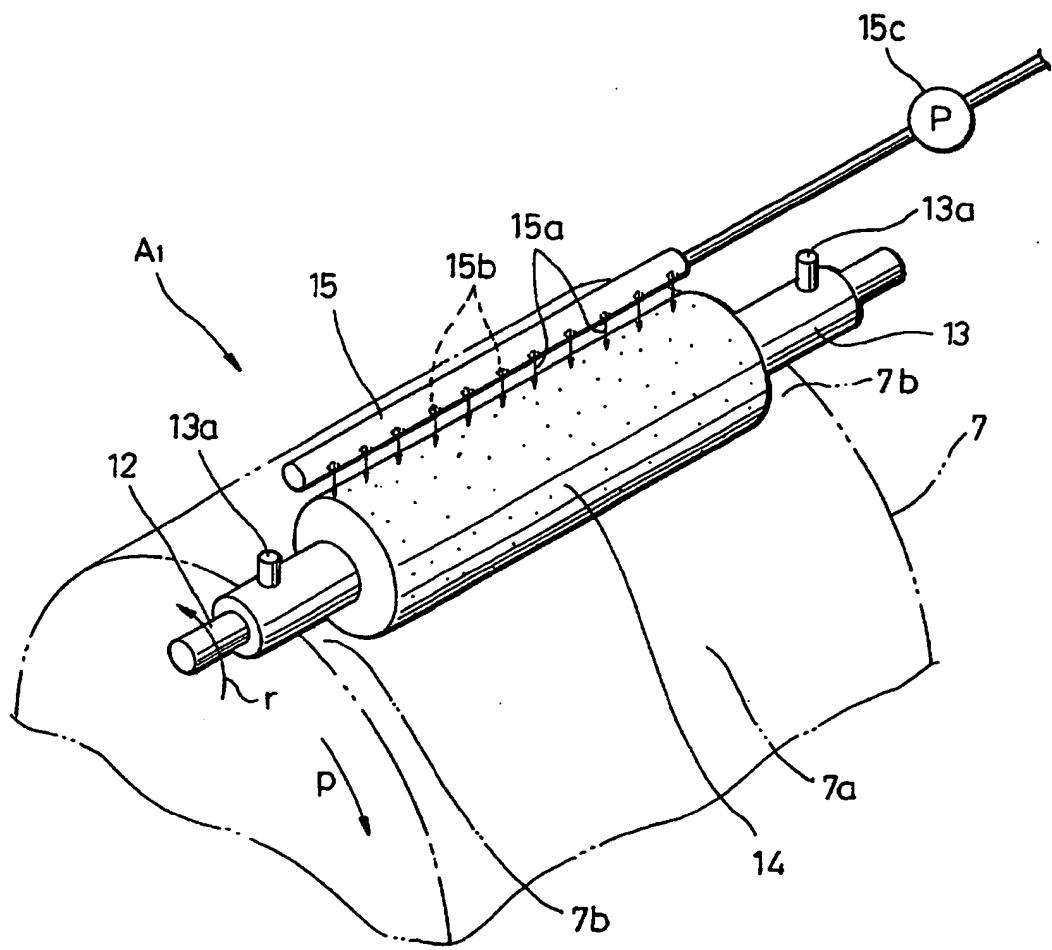


FIG. 6

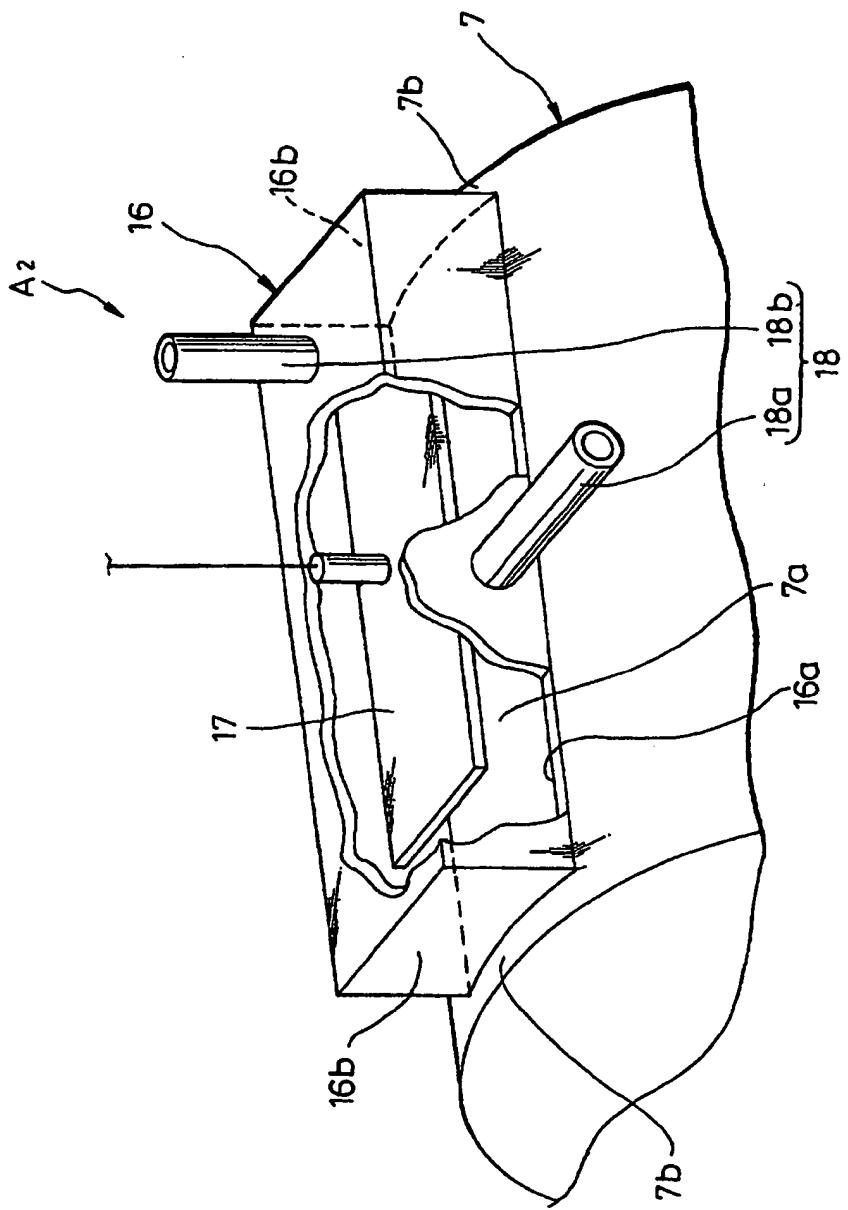


FIG. 7

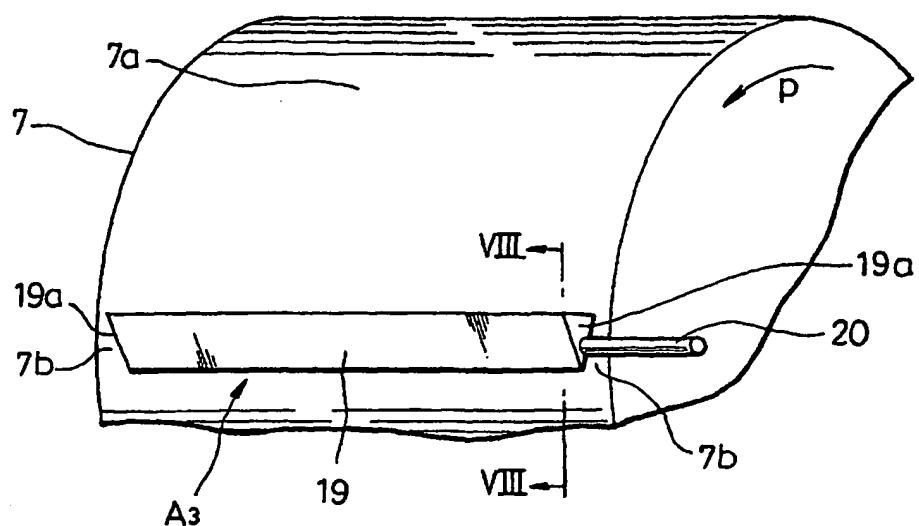


FIG. 8

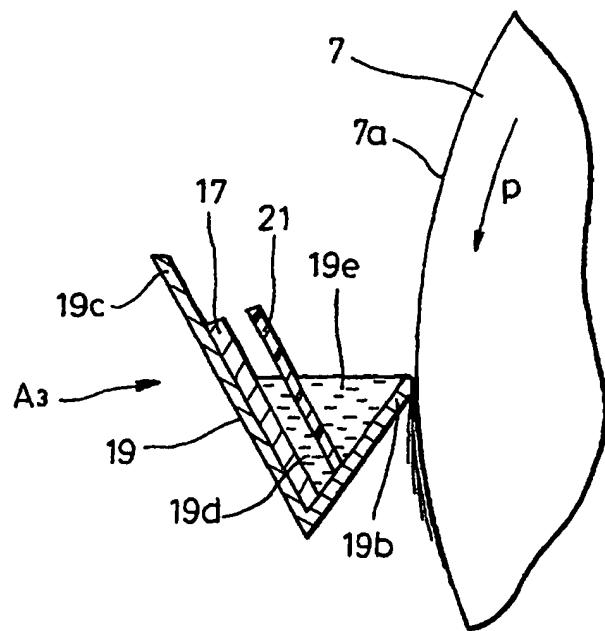


FIG. 9

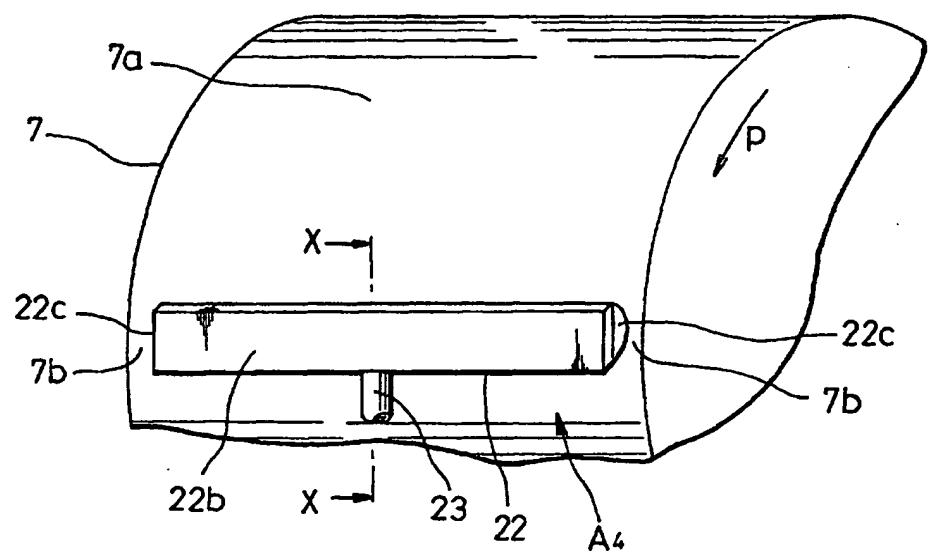


FIG. 10

